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(54) INK COMPOSITION AND INKJET RECORDING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an ink composition having excellent color reproducibility in printing, transparency, gloss, water resistance and image preservability; having excellent image fastness, for example, in image gloss and preservability against ozone in a specific combination with an image-receiving material; and having an improved abrasion resistance, and to provide an inkjet recording method using the ink composition.

SOLUTION: A solution containing a hydrophobic coloring matter, a hydrophobic polymer, a high boiling organic solvent having a solubility of water of ≤ 4 g, and a cosolvent having a boiling point of $\leq 20^{\circ}\text{C}$ and a solubility in water of ≤ 25 g, and an aqueous solvent are mixed to form an emulsion. Subsequently, the cosolvent is removed to obtain a colored fine particles. The ink composition contains the colored fine particles. The average particle diameter of the colored fine particles is $0.01\text{--}0.5\text{ }\mu\text{m}$, and a variation coefficient of the particle sizes is $\leq 45\%$. The specific gravity of the ink composition is $0.9\text{--}1.2$. The inkjet recording method comprises forming an image by shooting the ink composition on an ink receiving material, and subsequently, treating the colored fine particles by heating or pressing to fuse them.

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decision of rejection]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the ink jet record approach using the ink constituent containing hydrophobic coloring matter, and this ink constituent. The image excellent in scratch nature and robustness is related with the ink jet record approach using the ink constituent which can be formed by ink jet record, this ink constituent, and a television ingredient in more detail.

[0002]

[Description of the Prior Art] The approach of forming an image and an especially full color image is spreading quickly using recording methods, such as an ink jet method, an electrostatic image transfer method, and a sublimation mold hot printing method. In said recording method, a film photo is a target and it is the technical problem of development how color reproduction nature, an image consistency, gloss, a water resisting property, weatherability, etc. are brought especially close to silver salt color photography.

[0003] Said ink jet recording method makes the minute drop of ink fly by various working principles, is made to adhere to media for record, such as paper, and records an image, an alphabetic character, etc. the high-speed low noise and multiple-color-izing are easy for said ink jet recording method, its versatility of a record pattern is large, and development and fixing are unnecessary -- etc. -- it has the features. For this reason, as a recording method of the recording apparatus of various images, information machines and equipment are begun and said ink jet recording method has spread quickly in various kinds of applications. Furthermore, the image formed by the multicolor ink jet recording method is possible also for acquiring the record which is equal as compared with process printing by the platemaking method, and printing by the color photography method, and when there is few creation number of copies, since it can manufacture more cheaply than the usual process printing, it is being widely applied even to the full color image recording field. In said ink jet recording method, although amelioration of a recording device and the record approach has been performed with an improvement demand of recording characteristics, such as improvement in the speed of record, highly-minute-izing, and full-color-izing, an advanced property comes to be required also from ink or the medium for record, and various amelioration is performed that the engine performance exceeding silver salt color photography should be realized.

[0004] Some of the fundamental military requirements are satisfied by mainly using water soluble dye and using water soluble dye from a solvent object being aqueous, as a color material of the ink in an ink jet recording method, conventionally. However, when said water soluble dye is used and the record object originally printed since it was inferior to lightfastness or ozone resistance is saved for a long time, there are fading and problems, such as discoloring. Moreover, since a color is water solubility, the water resisting property of a record image poses a problem in many cases. That is, when a record image touches moisture, there is a fault that a record image spreads. Moreover, there are the glossiness of an image and a problem that it is not fully obtained. In an ink jet recording method, said trouble is a point which carries out a silver salt color photography pair, and is greatly inferior. In order to improve said trouble, the record medium of preparing the porous layer which consists of thermoplastic polymeric materials on a base material, dissolving a porous layer and carrying out eburnation according to an operation of heat and a pressure after printing is proposed by JP,58-136482,A and the U.S. Pat. No. 5,374,475 number specification.

[0005] Furthermore, the layer which consists of a thermoplastic latex is further prepared on the inorganic pigment layer which an ink absorbed amount becomes size, and coat-izing the thermoplastic latex layer of this outermost layer is indicated by JP,2-31673,B, JP,7-237348,A, and JP,8-2090,A after image formation.

[0006] However, in said conventional method, if the ink component remains in a latex layer when a latex layer is heated and coat-ized, on the front face of the coat which heat-treats a latex layer and is obtained, smooth nature good enough may not be obtained and glossiness may not fully be acquired. Moreover, a crack occurs on a coat for a residual solvent, and there is also a problem that the water resisting property of the part and weatherability fall.

[0007] On the other hand, recently, it changes to color ink, in order to solve lightfastness, ozone resistance, and a waterproof problem, the spread of pigment ink is made, and it is applied also to the ink jet recording method. However, pigment ink is hard to be referred to as enough, although surely lightfastness, a water resisting property, and ozone resistance are improved to some extent, and it is one side and it being inferior to color reproduction nature, since a pigment particle's has low transparency, and a pigment particle are hard, it exposes on the surface of a medium, there are problems, such as being inferior to scratch nature, and it has not resulted in the level of silver salt color photography at this point, either. Moreover, since accommodation of the specific gravity of a particle etc. is difficult for pigment ink, during preservation of ink, there is a problem of generating precipitate and the problem of own shelf life of ink is also inherent. Therefore, each advantage of said water-soluble ink and said pigment ink is provided, and the development of ink and the development of the image formation approach which improved each fault are called for.

[0008]

[Problem(s) to be Solved by the Invention] This invention solves many problems in said former, and makes it a technical problem to attain the following purposes. Namely, this invention is excellent in the color reproduction nature at the time of printing, transparency, and glossiness, excellent also in a water resisting property or image shelf life, further, with combination with a television ingredient, is excellent also in image robustness, such as the glossiness of an image, and a water resisting property, lightfastness, thermal resistance, ozone proof shelf life, and aims at offering the ink jet record approach using the ink constituent with which scratch nature was improved sharply, and this ink constituent.

[0009]

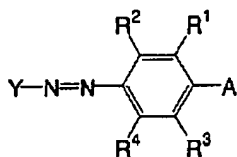
[Means for Solving the Problem] A means to solve said technical problem is as follows. Namely, <1> At least one sort of hydrophobic coloring matter, and at least one sort of hydrophobic polymers, At least 1 sort of high-boiling point organic solvent whose solubility of water is 4g or less, and the boiling point are 200 degrees C or less. And the solution containing at least one sort of auxiliary solvents whose solubility to water is 25g or less, And after mixing an aqueous medium and carrying out emulsification distribution, it is an ink constituent containing the coloring particle which removes said auxiliary solvent and is obtained. It is the ink constituent characterized by for the mean particle diameter of said coloring particle being 0.01-0.5 micrometers, and for the coefficient of variation of particle diameter being less than 45%, and specific gravity being 0.9-1.2.

[0010] <2> It is an ink constituent given in the above <1> of the compound chosen from the group which said hydrophobic coloring matter becomes from the compound expressed with the following general formula (I), the compound expressed with the following general formula (II), the compound expressed with the following general formula (Y-I), the compound expressed with the following general formula (M-I), and the compound expressed with the following general formula (C-I) which contains a kind at least.

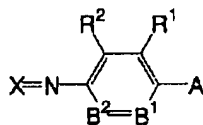
[0011]

[Formula 9]

一般式 (I)



一般式 (II)



In said general formula (I) and general formula (II) R1, R2, R3, and R4 Independently respectively A hydrogen atom, a halogen atom, an aliphatic series radical, an aromatic series radical, a heterocycle radical, A cyano group, a hydroxy group, a nitro group, the amino group, an alkylamino radical, An alkoxy group, an aryloxy group, an amide group, an arylamino radical, an ureido radical, A sulfamoylamino group, an alkylthio group, an aryl thio radical, an alkoxy carbonylamino radical, A sulfonamide radical, a carbamoyl group, a sulfamoyl group, a sulfonyl group, An alkoxy carbonyl group, a heterocycle oxy-radical, azo, an acyloxy radical, A carbamoyloxy radical, a silyloxy radical, an aryloxy carbonyl group, an aryloxy carbonylamine radical, an imide radical, a heterocycle thio radical, a sulfinyl group, a phosphoryl group, an acyl group, a carboxyl group, or a sulfonic group is expressed. A expresses -NR five R6 or a hydroxy group. R5 and R6 express a hydrogen atom, an aliphatic series radical, an aromatic series radical, and a heterocycle radical independently respectively. It may join together mutually and R5 and R6 may form the ring. B1 expresses =C(R3)- or =N-. B-2 expresses -C(R4) = or -N=. R1, R5, and R3 and R6 -- and/or, it may join together mutually and R1 and R2 may form an aromatic series ring or heterocycle.

[0012]

[Formula 10]

一般式 (Y-I)

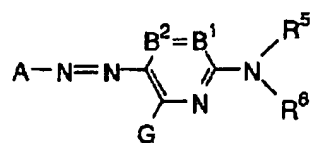
A-N=N-B

[0013] In said general formula (Y-I), A and B express respectively the heterocycle radical which may be permuted independently..

[0014]

[Formula 11]

一般式 (M-I)

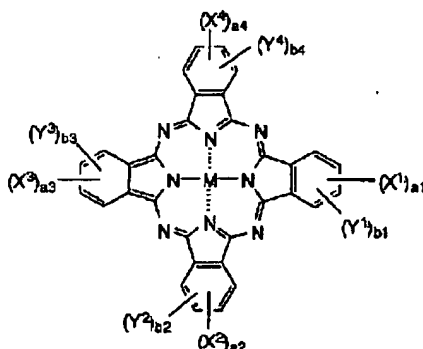


[0015] In said general formula (M-I), A expresses the residue of 5 member heterocycle diazo component A-NH2. B1 expresses =CR1-, B-2 expresses -CR2=, or either expresses a nitrogen atom and, as for B1 and B-2, another side expresses =CR1- or -CR2=. R5 and R6 express a hydrogen atom, an aliphatic series radical, an aromatic series radical, a heterocycle radical, an acyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a carbamoyl group, an alkyl sulfonyl group, an aryl sulfonyl group, or a sulfamoyl group independently respectively. Each radical may have the substituent further. G, R1, and R2 become independent respectively. A hydrogen atom, a halogen atom, an aliphatic series radical, An aromatic series radical, a heterocycle radical, a cyano group, a carboxyl group, a carbamoyl group, An alkoxy carbonyl group, an aryloxy carbonyl group, an acyl group, A hydroxy group, an alkoxy group, an aryloxy group, a silyloxy radical, An acyloxy radical, a carbamoyloxy radical, a heterocycle oxy-radical, alkoxy carbonyloxy group, The amino group permuted by aryloxy carbonyloxy group, the alkyl group, the aryl group, or the heterocycle radical, The acylamino radical, an ureido radical, a sulfamoylamino group, an alkoxy carbonylamino radical, An aryloxy carbonylamino radical, an alkyl aryl sulfonylamino radical, An aryl sulfonylamino radical, an aryloxy carbonylamino radical, A nitro group, an alkylthio group, an aryl thio radical, an alkyl sulfonyl group, an aryl sulfonyl group, an alkyl sulfinyl group, an aryl sulfinyl group, a sulfamoyl group, a sulfonic group, or a heterocycle thio radical is expressed. Each radical may be permuted further. R1, R5, or R5 and R6 may join together, and five to 6 membered-ring may be formed.

[0016]

[Formula 12]

一般式 (C-I)



[0017] In said general formula (C-I), X1, X2, X3, and X4 express -SO-Z1, -SO2-Z1, or -SO2NR 21R22 independently respectively. Z1 expresses the heterocycle radical which is not permuted [the aryl group which is not permuted / the aralkyl radical which is not permuted / the alkenyl radical which is not permuted / the cycloalkyl radical which is not permuted / the alkyl group which is not permuted / a permutation or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or]. R21 and R22 express respectively the heterocycle radical which is not permuted [the aryl group which is not permuted / the aralkyl radical which is not permuted / the alkenyl radical which is not permuted / the cycloalkyl radical which is not permuted / the alkyl group which is not permuted / a hydrogen atom, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or] independently. Respectively Y1, Y2, Y3, and Y4 independently A hydrogen atom, a halogen atom, An alkyl group, a cycloalkyl radical, an alkenyl radical, an aralkyl radical, an aryl group, A heterocycle radical, a cyano group, hydroxyl, a nitro group, the amino group, an alkylamino radical, An alkoxy group, an aryloxy group, an amide group, an arylamino radical, an ureido radical, A sulfamoylamino group, an alkylthio group, an aryl thio radical, an alkoxy carbonylamino radical, A sulfonamide radical, a carbamoyl group, a sulfamoyl group, a sulfonyl group, An alkoxy carbonyl group, a heterocycle oxy-radical, azo, an acyloxy radical, A carbamoyloxy radical, a silyloxy radical, an aryloxy carbonyl group, an aryloxy carbonylamino radical, an imide radical, a heterocycle thio radical, a phosphoryl

group, an acyl group, a carboxyl group, or a sulfonic group may be expressed, and each may have the substituent further. a1-a4, and b1-b4 express the number of substituents of X1-X4, and Y1-Y4 respectively, a1-a4 express the integer of 0-4 independently respectively, and b1-b4 express the integer of 0-4 independently respectively. However, total of a1-a4 is two or more. Here, when a1-a4, and b1-b4 express two or more integers, even if two or more X1-X4, and Y1-Y4 are respectively the same, they may differ. a1 and b1 express the integer with which the relation of $a1+b1=4$ is filled and which is independent 0-independent 4 respectively. a2 and b2 express the integer with which the relation of $a2+b2=4$ is filled and which is independent 0-independent 4 respectively. a3 and b3 express the integer with which the relation of $a3+b3=4$ is filled and which is independent 0-independent 4 respectively. a4 and b4 express the integer with which the relation of $a4+b4=4$ is filled and which is independent 0-independent 4 respectively. M expresses a hydrogen atom, a metallic element or its oxide, a hydroxide, or a halogenide.

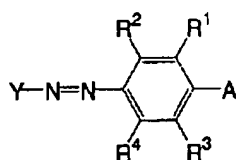
[0018] <3> It is the ink-jet record approach which records using the ink constituent which contains the coloring particle containing at least one sort of hydrophobic coloring matter, and at least one sort of hydrophobic polymers to an ink television ingredient, and it is the ink-jet record approach characterized for said coloring particle by heat-treatment and/or to carry out pressure treatment and to carry out welding of said coloring particle after forming an image by reaching the target said ink constituent on said television ingredient.

[0019] <4> Said hydrophobic coloring matter is the ink jet record approach given in the above <3> of the compound expressed with the following general formula (I), the compound expressed with the following general formula (II), the compound expressed with the following general formula (Y-I), the compound expressed with the following general formula (M-I), and the compound chosen from the group which it becomes from that of a compound which is expressed with the following general formula (C-I) which contains a kind at least.

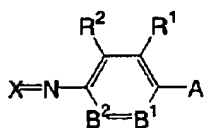
[0020]

[Formula 13]

一般式 (I)



一般式 (II)

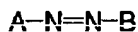


[0021] In said general formula (I) and general formula (II) R1, R2, R3, and R4 Independently respectively A hydrogen atom, a halogen atom, an aliphatic series radical, an aromatic series radical, a heterocycle radical, A cyano group, a hydroxy group, a nitro group, the amino group, an alkylamino radical, An alkoxy group, an aryloxy group, an amide group, an arylamino radical, an ureido radical, A sulfamoylamino group, an alkylthio group, an aryl thio radical, an alkoxy carbonylamino radical, A sulfonamide radical, a carbamoyl group, a sulfamoyl group, a sulfonyl group, An alkoxy carbonyl group, a heterocycle oxy-radical, azo, an acyloxy radical, A carbamoyloxy radical, a silyloxy radical, an aryloxy carbonyl group, an aryloxycarbonylamine radical, an imide radical, a heterocycle thio radical, a sulfinyl group, a phosphoryl group, an acyl group, a carboxyl group, or a sulfonic group is expressed. A expresses -NR five R6 or a hydroxy group. R5 and R6 express a hydrogen atom, an aliphatic series radical, an aromatic series radical, and a heterocycle radical independently respectively. It may join together mutually and R5 and R6 may form the ring. B1 expresses =C(R3)- or =N-. B-2 expresses -C(R4) = or -N=. R1, R5, and R3 and R6 -- and/or, it may join together mutually and R1 and R2 may form an aromatic series ring or heterocycle.

[0022]

[Formula 14]

一般式 (Y-I)

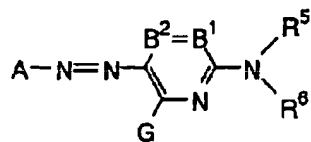


[0023] In said general formula (Y-I), A and B express respectively the heterocycle radical which may be permuted independently.

[0024]

[Formula 15]

一般式 (M-I)



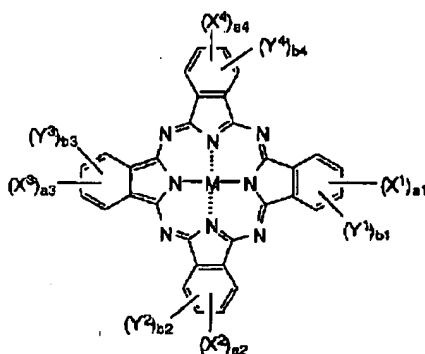
[0025] In said general formula (M-I), A expresses the residue of 5 member heterocycle diazo component A-NH2. B1 expresses =CR1-, B-2 expresses -CR2=, or either expresses a nitrogen atom and, as for B1 and B-2, another side

expresses =CR1- or -CR2=. R5 and R6 express a hydrogen atom, an aliphatic series radical, an aromatic series radical, a heterocycle radical, an acyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a carbamoyl group, an alkyl sulfonyl group, an aryl sulfonyl group, or a sulfamoyl group independently respectively. Each radical may have the substituent further. G, R1, and R2 become independent respectively. A hydrogen atom, a halogen atom, an aliphatic series radical, An aromatic series radical, a heterocycle radical, a cyano group, a carboxyl group, a carbamoyl group, An alkoxy carbonyl group, an aryloxy carbonyl group, an acyl group, A hydroxy group, an alkoxy group, an aryloxy group, a silyloxy radical, An acyloxy radical, a carbamoyloxy radical, a heterocycle oxy-radical, alkoxy carbonyloxy group, The amino group permuted by aryloxy carbonyloxy group, the alkyl group, the aryl group, or the heterocycle radical, The acylamino radical, an ureido radical, a sulfamoylamino group, an alkoxycarbonylamino radical, An aryloxycarbonylamine radical, an alkyl aryl sulfonylamino radical, An aryl sulfonylamino radical, an aryloxycarbonylamine radical, A nitro group, an alkylthio group, an aryl thio radical, an alkyl sulfonyl group, an aryl sulfonyl group, an alkyl sulfinyl group, an aryl sulfinyl group, a sulfamoyl group, a sulfonic group, or a heterocycle thio radical is expressed. Each radical may be permuted further. R1, R5, or R5 and R6 may join together, and five to 6 membered-ring may be formed.

[0026]

[Formula 16]

一般式 (C-I)



[0027] In said general formula (C-I), X1, X2, X3, and X4 express -SO-Z1, -SO2-Z1, or -SO2NR21R22 independently respectively. Z1 expresses the heterocycle radical which is not permuted [the aryl group which is not permuted / the aralkyl radical which is not permuted / the alkenyl radical which is not permuted / the cycloalkyl radical which is not permuted / the alkyl group which is not permuted / a permutation or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or]. R21 and R22 express respectively the heterocycle radical which is not permuted [the aryl group which is not permuted / the aralkyl radical which is not permuted / the alkenyl radical which is not permuted / the cycloalkyl radical which is not permuted / the alkyl group which is not permuted / a hydrogen atom, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or] independently. Respectively Y1, Y2, Y3, and Y4 independently A hydrogen atom, a halogen atom, An alkyl group, a cycloalkyl radical, an alkenyl radical, an aralkyl radical, an aryl group, A heterocycle radical, a cyano group, hydroxyl, a nitro group, the amino group, an alkylamino radical, An alkoxy group, an aryloxy group, an amide group, an arylamino radical, an ureido radical, A sulfamoylamino group, an alkylthio group, an aryl thio radical, an alkoxycarbonylamino radical, A sulfonamide radical, a carbamoyl group, a sulfamoyl group, a sulfonyl group, An alkoxy carbonyl group, a heterocycle oxy-radical, azo, an acyloxy radical, A carbamoyloxy radical, a silyloxy radical, an aryloxy carbonyl group, an aryloxycarbonylamine radical, an imide radical, a heterocycle thio radical, a phosphoryl group, an acyl group, a carboxyl group, or a sulfonic group may be expressed, and each may have the substituent further. a1-a4, and b1-b4 express the number of substituents of X1-X4, and Y1-Y4 respectively, a1-a4 express the integer of 0-4 independently respectively, and b1-b4 express the integer of 0-4 independently respectively. However, total of a1-a4 is two or more. Here, when a1-a4, and b1-b4 express two or more integers, even if two or more X1-X4, and Y1-Y4 are respectively the same, they may differ. a1 and b1 express the integer with which the relation of a1+b1=4 is filled and which is independent 0-independent 4 respectively. a2 and b2 express the integer with which the relation of a2+b2=4 is filled and which is independent 0-independent 4 respectively. a3 and b3 express the integer with which the relation of a3+b3=4 is filled and which is independent 0-independent 4 respectively. a4 and b4 express the integer with which the relation of a4+b4=4 is filled and which is independent 0-independent 4 respectively. M expresses a hydrogen atom, a metallic element or its oxide, a hydroxide, or a halogenide.

[0028] <5> As opposed to said television ingredient which has at least one-layer porosity resin layer containing a thermoplastic hydrophobic polymer particle on a base material It is the ink jet record approach which records using the

ink constituent containing the coloring particle containing at least one sort of hydrophobic coloring matter, and at least one sort of hydrophobic polymers. It is the ink jet record approach of heat-treatment and/or the above <3> to which pressure treatment is carried out and welding of said coloring particle is carried out, or the publication to <4> of said coloring particle and a porosity resin layer after forming an image by reaching the target said ink constituent on said television ingredient.

[0029] <6> The mean particle diameter of said thermoplastic hydrophobic polymer particle is the ink jet record approach given in the larger above <5> than the mean particle diameter of said coloring particle.

[0030] <7> The relation between the mean particle diameter d_1 (micrometer) of said coloring particle and the mean particle diameter d_2 (micrometer) of said thermoplastic hydrophobic polymer particle is the ink jet record approach given in the above <6> which is $2 < d_2/d_1 < 100$.

[0031] <8> Said thermoplastic hydrophobic polymer particle and the hydrophobic polymer contained in said coloring particle are the ink jet record approaches given in either of <7> from the above <5> which has at least one sort of common monomer units mutually.

[0032] <9> Said ink constituent is the ink jet record approach given in either of <8> from the above <4> which is the above <1> or an ink constituent given in <2>.

[0033]

[Embodiment of the Invention] Hereafter, the ink constituent and the ink jet record approach of this invention are explained.

[0034] The ink constituent of this invention At least one sort of hydrophobic coloring matter, (Ink constituent) At least one sort of hydrophobic polymers, and at least one sort of high-boiling point organic solvents whose solubility of water is 4g or less, The solution containing at least one sort of auxiliary solvents whose boiling points are 200 degrees C or less and whose solubility to water is 25g or less, And after mixing an aquosity medium and carrying out emulsification distribution, it is characterized by containing the coloring particle which removes said auxiliary solvent and is obtained, for the mean particle diameter of said coloring particle being 0.01-0.5 micrometers, and for the coefficient of variation of particle diameter being less than 45%, and specific gravity being 0.9-1.2. It is desirable to contain [of the compound chosen from the group which consists of the compound expressed with the general formula (I) mentioned later as said hydrophobic coloring matter, the compound expressed with a general formula (II), the compound expressed with a general formula (Y-I), a compound expressed with a general formula (M-I), and a compound expressed with a general formula (C-I)] a kind at least.

[0035] Said coloring particle is a transparent very fine particle which contains at least one sort of hydrophobic coloring matter, and at least one sort of hydrophobic polymers at least, and as long as it dissolves mutually, it may prepare said hydrophobic coloring matter and said hydrophobic polymer by what kind of approach. However, it is difficult to infiltrate said coloring matter into homogeneity using the organic solvent with which it mixes with water, such as an acetone, by the approach of the so-called loader bull latex of infiltrating hydrophobic coloring matter into aquosity polymeric latex. After, mixing the solution containing hydrophobic coloring matter, a hydrophobic polymer, a water-insoluble nature high-boiling point organic solvent, and an auxiliary solvent, and an aquosity medium on the other hand and carrying out emulsification distribution, according to the preparation approach concerning this invention which removes said auxiliary solvent, the coloring particle of stable this invention is obtained. Under the present circumstances, prediction of the compatibility of the target coloring particle, specific gravity, and hardness is possible by investigating the sample of the coloring particle which prepares the solution to which the class and amount of a constituent in this solution were changed beforehand, removes an auxiliary solvent by volatilization etc., and is obtained.

[0036] In addition, the "aquosity medium" in this invention means what added additives, such as a surfactant, a stabilizer, and antiseptics, into the mixture of water, or a little water miscibility organic solvent and water if needed.

[0037] <Hydrophobic coloring matter> Here, the hydrophobic coloring matter contained to said coloring particle is explained. The hydrophobic coloring matter which is one of the components which constitute the coloring particle of this invention means insoluble coloring matter substantially in water. The solubility (mass of the coloring matter which can dissolve in 100g of water) to 25-degree C water is 1g or less, and, more specifically, 0.5g or less of things which are 0.1g or less more preferably is meant preferably. Therefore, hydrophobic coloring matter means an insoluble pigment and oil solubility coloring matter in the so-called water, and oil solubility coloring matter is more desirable also in it.

[0038] As said hydrophobic coloring matter, a thing 200 degrees C or less has the desirable melting point, that whose melting point is 150 degrees C or less is more desirable, and that whose melting point is 100 degrees C or less still more desirable. By using hydrophobic coloring matter with the low melting point, a crystal deposit of the coloring matter in the inside of an ink constituent is controlled, and the preservation stability of an ink constituent becomes good. In the ink constituent of this invention, hydrophobic coloring matter may be used by the one-sort independent,

and some kinds may be mixed and used. Moreover, coloring matters, such as other water soluble dye, a disperse dye, and a pigment, may contain in the range which does not check the effectiveness of this invention if needed.

[0039] As usable hydrophobic coloring matter, an anthraquinone system, a naphthoquinone system, a styryl system, the India aniline system, an azo system, a nitroglycerine system, a coumarin system, a methine system, a porphyrin system, an aza-porphyrin system, phthalocyanine system coloring matter, etc. are mentioned to the ink constituent of this invention, for example. In addition, in order to make it complete as ink jet ink for full color printing, the coloring matter of at least 4 colors which added black is usually needed for the three primary colors of yellow (Y), a Magenta (M), and cyanogen (C).

[0040] As yellow coloring matter, the thing of arbitration can be used for this invention among usable hydrophobic coloring matter. As a coupling component, for example, phenols, naphthols, aniline, Pyrazolones and pyridone Methine dye [, such as azomethine color; for example, a benzylidene color, which has opening-and-closing mold activity methylene compounds as aryl or HETERIRUAZO color; for example, a coupling component, which has opening-and-closing mold activity methylene compounds, and a mono-methine oxo-Norian color]; for example, a naphthoquinone color, There are quinone system colors, such as anthraquinone dye, etc. and a kino FUTARON color, nitroglycerine nitroso dye, acridine dye, an AKURIJINON color, etc. can be mentioned as color kinds other than this.

[0041] As Magenta coloring matter, the thing of arbitration can be used for this invention among usable hydrophobic coloring matter. As aryl or HETERIRUAZO color; for example, a coupling component, which has phenols, naphthols, and aniline as a coupling component, for example, pyrazolones Azomethine color; for example, an ARIRIDEN color, which has pyrazolo triazoles Methine dye like a styryl color, a merocyanine color, and an oxo-Norian color; Diphenylmethane dye, Condensed multi-ring system colors, such as quinone system colors, for example, a dioxazine color etc., such as triphenylmethane dye and a carbonium color like xanthene dye, for example, a naphthoquinone, anthraquinone, and anthra pyridone, etc. can be mentioned.

[0042] As cyanogen coloring matter, the thing of arbitration can be used for this invention among usable hydrophobic coloring matter. For example, Pori methine dye; diphenylmethane dye like the azomethine color; cyanine dye which has pyrrolo triazoles as India aniline dye, indophenol dye, or a coupling component, an oxo-Norian color, and a merocyanine color, triphenylmethane dye, carbonium color; phthalocyanine dye like xanthene dye; the aryl which has phenols, naphthols, and aniline as anthraquinone dye; for example, a coupling component, or a HETERIRUAZO color, and an indigo thioindigo color can be mentioned.

[0043] Each aforementioned color may present each color of yellow, a Magenta, and cyanogen only after some KUROMO forehands may dissociate it, and the counter cations in that case may be alkali metal and an inorganic cation like ammonium, may be organic cations like pyridinium and quaternary ammonium salt, and may be polymer cations which have them in a substructure further.

[0044] Although the following are mentioned as a desirable example also in said hydrophobic coloring matter, this invention is not limited to these at all. For example C. I. solvent blacks 3, 7, 27, and 29 And the 34; C.I. solvent yellow 14, 16, 19, 29, 30, 56, 82, and 93 and 162; C.I. solvent red 1, 3, 8, 18, 24, 27, 43, 49, 51, 72, and 73, 109, 122, 132 And the 218; C.I. solvent violet 3; C.I. solvent blues 2, 11, 25, 35, 38, and 67 and 70; C.I. solvent Green 3 and 7; C.I. solvent Orange 2 grade is desirable in a list. Also in these, it is Nubian. Black PC-0850, Oil Black HBB, Oil Yellow 129, Oil Yellow 105, Oil Pink 312, Oil Red 5B, Oil Scarlet 308, Vali Fast Blue 2606, Oil Blue BOS (product made from ORIENT Chemistry), Aizen Spilon Blue GNH (product made from Hodogaya Chemistry), Neopen Yellow 075, Neopen Mazenta SE1378, Neopen Blue 808, Neopen Blue FF4012, Neopen Cyan FF4238 (BASF A.G. make) etc. is more desirable.

[0045] Moreover, in this invention, although a disperse dye can also be used in the range dissolved in a water-immiscible organic solvent and the following are mentioned as the desirable example, this invention is not limited to these at all. For example C. I. De Dis parsing yellow 5, 42, 54, 64, 79, 82, 83, 93, 99, 100, 119, and 122, 124, 126, 160, 184:1, 186, 198 and 199, 201, 204, 224, and the 237; C.I. De Dis parsing oranges 13 and 29, 31: 1, 33, 49, 54, 55, 66, 73, 118, 119 And 163; C. I. De Dis parsing red 54, 60, 72, 73, 86, 88, 91, 92, 93, 111, 126, 127, 134, 135, 143, 145, 152, and 153, 154, 159, 164, 167:1, 177, 181, 204, 206, 207, 221, 239, 240, 258, 277, 278, 283, 311, 323, 343, 348, 356, and the 362; C.I. De Dis parsing violet 33; C.I. De Dis parsing blues 56, 60, 73, 87, 113, 128, 143, 148, 154, 158, and 165, 165:1, 165:2, 176, 183, 185, 197, 198, 201, 214, 224, 225, 257, 266, 267, 287, 354, 358, 365 and 368; the C.I. De Dis parsing green 6:1 and 9 grades are desirable in a list.

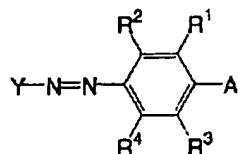
[0046] Moreover, the compound (azo dye) expressed with the following general formula (I) and the compound (azomethine color) expressed with the following general formula (II) are suitably mentioned also in said hydrophobic coloring matter. The azomethine color expressed with the following general formula (II) is known in the photograph ingredient as a color generated by oxidation from a coupler and a developing agent. In addition, although the compound expressed with a general formula (I) and a general formula (II) below is explained, the compound whose at least one of each radicals of the following general formula (I) and a general formula (II) is the desirable range shown below is desirable, the compound more whose radicals are desirable range is more desirable, and especially the

compound all whose radicals are desirable range is desirable.

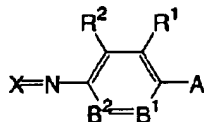
[0047]

[Formula 17]

一般式 (I)



一般式 (II)



[0048] In said general formula (I) and general formula (II) R1, R2, R3, and R4 Independently respectively A hydrogen atom, a halogen atom, an aliphatic series radical, an aromatic series radical, a heterocycle radical, A cyano group, a hydroxy group, a nitro group, the amino group, an alkylamino radical, An alkoxy group, an aryloxy group, an amide group, an arylamino radical, an ureido radical, A sulfamoylamino group, an alkylthio group, an aryl thio radical, an alkoxy carbonylamino radical, A sulfonamide radical, a carbamoyl group, a sulfamoyl group, a sulfonyl group, An alkoxy carbonyl group, a heterocycle oxy-radical, azo, an acyloxy radical, A carbamoyloxy radical, a silyloxy radical, an aryloxy carbonyl group, an aryloxy carbonylamine radical, an imide radical, a heterocycle thio radical, a sulfinyl group, a phosphoryl group, an acyl group, a carboxyl group, or a sulfonic group is expressed. Also in these, a hydrogen atom, a halogen atom, an aliphatic series radical, an alkoxy group, an aryloxy group, an amide group, an ureido radical, a sulfamoylamino group, an alkoxy carbonylamino radical, and a sulfonamide radical are desirable as R2.

[0049] In said general formula (I) and general formula (II), A expresses -NR five R6 or a hydroxy group. As A, -NR five R6 is desirable. Said R5 and R6 express a hydrogen atom, an aliphatic series radical, an aromatic series radical, and a heterocycle radical independently respectively. As said R5 and R6, a hydrogen atom, an alkyl group and a permutation alkyl group, an aryl group, and a permutation aryl group are more desirable, and the alkyl group and carbon atomic number of 1-18 have [a hydrogen atom and a carbon atomic number] the permutation alkyl group of 1-18 respectively most desirable also in it, independently. It may join together mutually and R5 and R6 may form the ring.

[0050] In said general formula (II), B1 expresses =C(R3)- or =N-. B-2 expresses -C(R4) = or =N-. B1 and B-2 are in coincidence. - The case where it does not become N= is desirable and the case where B1 becomes =C(R3)- and B-2 becomes -C(R4) = is more desirable.

[0051] said general formula (I) and general formula (II) -- setting -- R1, R5, and R3 and R6 -- and/or, it may join together mutually and R1 and R2 may form an aromatic series ring or heterocycle.

[0052] In this specification, an aliphatic series radical means an alkyl group, a permutation alkyl group, an alkenyl radical, a permutation alkenyl radical, an alkynyl group, a permutation alkynyl group, an aralkyl radical, and a permutation aralkyl radical. Said aliphatic series radical may be a letter of branching, and may be annular. As for the carbon atomic number in said aliphatic series radical, 1-20 are desirable, and 1-18 are more desirable. The aryl parts of said aralkyl radical and a permutation aralkyl radical have a phenyl group and a desirable naphthyl group, and its phenyl group is more desirable. The thing same as a substituent of the alkyl part in said permutation alkyl group, a permutation alkenyl radical, a permutation alkynyl group, and a permutation aralkyl radical as the example of the substituent mentioned by said R1, R2, R3, and R4 is mentioned. The thing same as a substituent of the aryl part in said permutation aralkyl radical as the example of the substituent in the following permutation aryl group is mentioned.

[0053] In this specification, an aromatic series radical means an aryl group and a permutation aryl group. As said aryl group, a phenyl group and a naphthyl group are desirable, and a phenyl group is more desirable. The aryl part in said permutation aryl group is the same as that of the case of the above-mentioned aryl group. The thing same as a substituent in said permutation aryl group as the example of the substituent mentioned by said R1, R2, R3, and R4 is mentioned.

[0054] In said general formula (I), Y expresses a partial saturation heterocycle radical. As Y, the partial saturation heterocycle of 5 members or 6 members is desirable. In heterocycle, an aliphatic series ring, an aromatic series ring, or other heterocycles may condense. N, O, and S can be mentioned as an example of the hetero atom of heterocycle. As said partial saturation heterocycle, a pyrazole ring, an imidazole ring, a thiazole ring, an iso thiazole ring, a thiadiazole ring, a thiophene ring, a benzothiazole ring, a benzooxazole ring, a benzoISOCHI azole ring, a pyrimidine ring, a pyridine ring, a quinoline ring, etc. are desirable, for example. Moreover, said partial saturation heterocycle radical may have the substituent mentioned by said R1-R4.

[0055] In said general formula (II), X expresses the residue of a color photography coupler. As said coupler, the following couplers are desirable. As a yellow coupler, a U.S. Pat. No. 3,933,501 number, said 4,022,620 numbers, Said 4,326,024 numbers, said 4,401,752 numbers, said 4,248,961 numbers, JP,58-10739,B, British JP,1,425,020,B, said 1,476,760 numbers, A U.S. Pat. No. 3,973,968 number, said 4,314,023 numbers, said 4,511,649 numbers, The coupler

expressed with the formula (I) of Europe JP,249,473,B No. A and these 502,424A numbers, and (II), The coupler expressed with the formula (1) of these 513,496A numbers, and (2) (especially Y-28 [18-page]), The coupler expressed with the formula (I) of the claim 1 of these 568,037A numbers, The coupler expressed with the general formula of 45-55 lines of the column 1 of a U.S. Pat. No. 5,066,576 number (I), The coupler expressed with the general formula (I) of the paragraph 0008 of JP,4-274425,A, A coupler given in the Europe JP,498,381,B A1 No. claim [40-page] 1 (especially D-35 [18-page]), said -- the coupler (especially) expressed with the 4-page formula (Y) of No. 447,969A1 The coupler (especially II- 17, 19 (column 17), II- 24 (column 19)) expressed with formula (II) of 36-58 lines of the column 7 of Y-1 (17 pages), Y-54 (41 pages), and a U.S. Pat. No. 4,476,219 number - (IV) is mentioned. [0056] As a Magenta coupler, a U.S. Pat. No. 4,310,619 number, said 4,351,897 numbers, Europe JP,73,636,B, a U.S. Pat. No. 3,061,432 number, said 3,725,067 numbers, Research disclosure No.24220 (June, 1984), said -- No.24230 (June, 1984) and JP,60-33552,A -- 60-43659, 61-72238, 60-35730, 55-118034, 60-185951, a U.S. Pat. No. 4,500,630 number, Said 4,540,654 numbers, said 4,556,630 numbers, the international public presentation WO 88/No. 04795, JP,3-39737,A (L-57 (11-page lower right) and L-68 (12-page lower right) --) L-77 (13-page lower right), [A-4]-63 of Europe JP,456,257,B (134 pages), [A-4] -73 and -75 (139 pages) -- said -- M-4 of No. 486,965, and -6 (26 pages) -- The M-22 grade of the paragraph 0237 of 4-362631 of M-7 (27 pages), M-45 (19 pages) of these 571,959A numbers, and JP,5-204106,A (6 (M-1) pages) is mentioned.

[0057] As a cyan coupler, a U.S. Pat. No. 4,052,212 number, said 4,146,396 numbers, Said 4,228,233 numbers, said 4,296,200 numbers, Europe JP,73,636,B, CX-1 of JP,4-204843,A, 3, 4, 5, 11, 12 and 14, and C- of 15(14-16 pages); JP,4-43345,A -- 7 and 10 (35 pages) -- 34, 35 (37 pages), (I-1); (42 (I-17)-43 pages) the coupler expressed with the general formula (Ia) of claim 1 of JP,6-67385,A or (Ib) is mentioned.

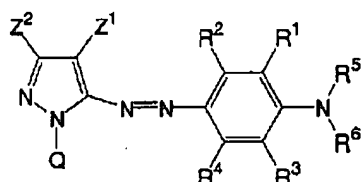
[0058] In addition, a coupler given in JP,62-215272,A (91 pages), JP,2-33144,A (3-page, 30 pages), and EP355,660A (4 pages, 5 pages, 45 pages, 47 pages) is also useful.

[0059] Also in the color expressed with said general formula (I), the color expressed with the following general formula (III) is especially desirable as a Magenta color.

[0060]

[Formula 18]

一般式 (III)



[0061] In said general formula (III), as for Z1, Hammett's substituent constant sigma_p value expresses 0.20 or more electronic suction nature machines. As Z1, 1.0 or less or more 0.30 electronic suction nature machine has desirable sigma_p value. Although the electron withdrawing substituent mentioned later can be mentioned as a desirable concrete substituent Also in it, the acyl group of carbon numbers 2-12, the alkyloxy carbonyl group of carbon numbers 2-12, A nitro group, a cyano group, the alkyl sulfonyl group of carbon numbers 1-12, the aryl sulfonyl group of carbon numbers 6-18, The carbamoyl group of carbon numbers 1-12 and the alkyl halide radical of carbon numbers 1-12 are more desirable, a cyano group, the alkyl sulfonyl group of carbon numbers 1-12, and the aryl sulfonyl group of carbon numbers 6-18 are still more desirable, and especially a cyano group is desirable.

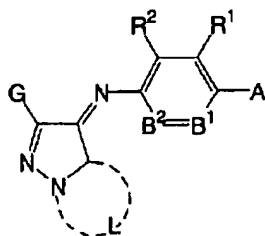
[0062] R1-R6 are synonymous with said general formula (I). Z2 expresses a hydrogen atom, an aliphatic series radical, or an aromatic series radical. Q expresses a hydrogen atom, an aliphatic series radical, an aromatic series radical, or a heterocycle radical. Also in it, the radical which consists of a nonmetal atom group required as Q to form five membered-rings - 8 membered-ring is desirable, and an aromatic series radical or a heterocycle radical is more desirable. Said five membered-rings - 8 membered-ring may be permuted, and even if it is a saturation ring, it may have the unsaturated bond. As said nonmetal atom group, a nitrogen atom, an oxygen atom, a sulfur atom, or a carbon atom is desirable. As said five membered-rings - 8 membered-ring, for example The benzene ring, a cyclopentane ring, A cyclohexane ring, a cycloheptane ring, a cyclooctane ring, a cyclohexene ring, A pyridine ring, a pyrimidine ring, a pyrazine ring, a pyridazine ring, a triazine ring, When an imidazole ring, a benzimidazole ring, an oxazole ring, a benzoxazole ring, an oxane ring, a sulfolane ring, the Jiang ring, etc. are mentioned suitably and these rings have a substituent further, as this substituent, the radical illustrated by said R1-R4 is desirable. In addition, as desirable structure of a color expressed with said general formula (III), an application for patent No. 220649 [2000 to] has a publication.

[0063] Also in the color expressed with said general formula (II), the color expressed with the following general formula (IV) is especially desirable as a Magenta color.

[0064]

[Formula 19]

一般式 (IV)



[0065] In said general formula (IV), G expresses a hydrogen atom, an aliphatic series radical, an aromatic series radical, a heterocycle radical, a cyano group, an alkoxy group, an aryloxy group, an alkylthio group, an aryl thio radical, an ester group, the amino group, a carbamoyl group, a sulfonyl group, a sulfamoyl group, an ureido radical, a urethane group, an acyl group, an amide group, or a sulfonamide radical. Moreover, R1, R2, A, B1, and B-2 are synonymous with said general formula (II), and those desirable range of them is the same as that of said general formula (II). The atomic group which L expresses the atomic group which forms the nitrogen-containing heterocycle of 5 members or 6 members, and forms this nitrogen-containing heterocycle An aliphatic series radical, an aromatic series radical, a heterocycle radical, a cyano group, an alkoxy group, an aryl group, An oxy-radical, an alkylthio group, an aryl thio radical, an ester group, the amino group, You may permute by at least one of a carbamoyl group, a sulfonyl group, a sulfamoyl group, an ureido radical, a urethane group, an acyl group, an amide group, or sulfonamide radicals, and still more nearly another ring and condensed ring may be formed.

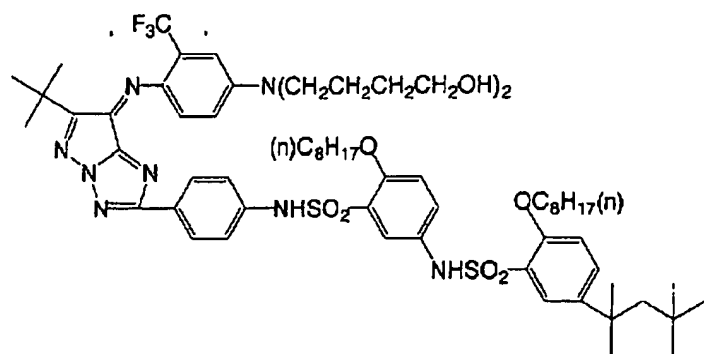
[0066] As A, as L, it is desirable to form the nitrogen-containing heterocycle of 5 members, and an imidazole ring, a triazole ring, a tetrazole ring, etc. are desirable [-NR five R6 is desirable, and] in the color expressed with said general formula (IV), as nitrogen-containing heterocycle of 5 members, for example.

[0067] Next, although the instantiation compound (M-1-70) of a Magenta color is shown below among the colors expressed with said general formula (I) and said general formula (II), this invention is not limited at all by these.

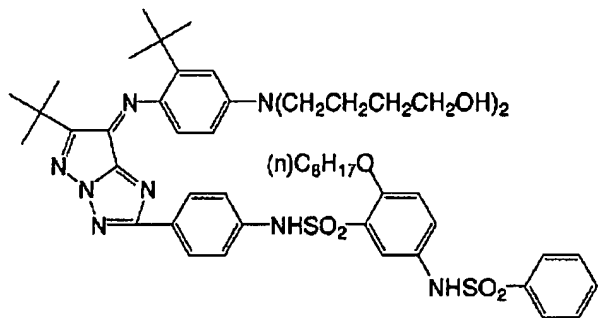
[0068]

[Formula 20]

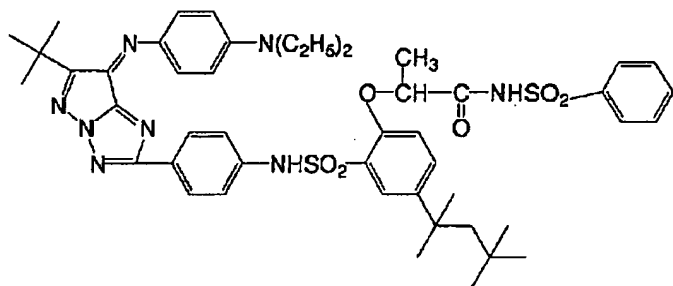
M - 1



M - 2



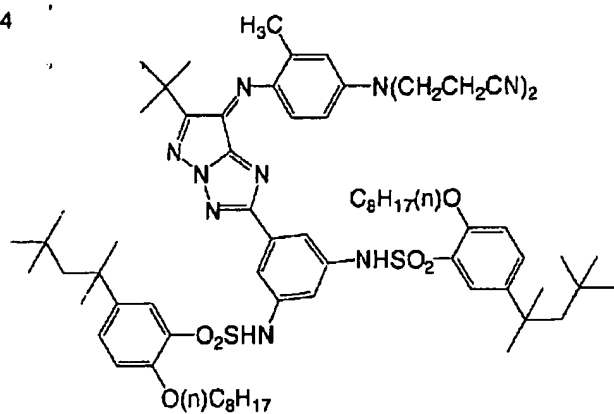
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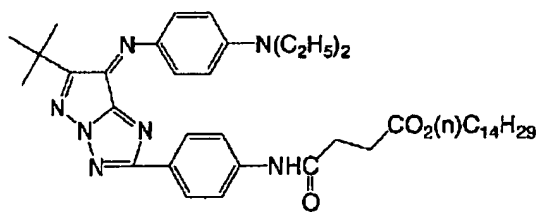
[0069]

[Formula 21]

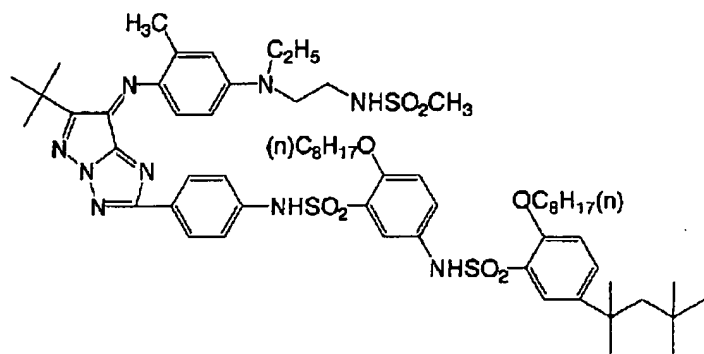
M - 4



M - 5



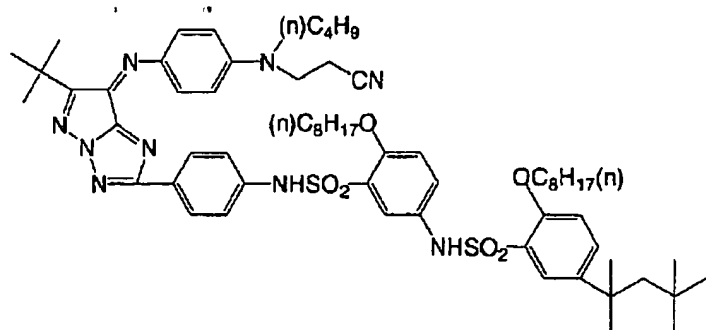
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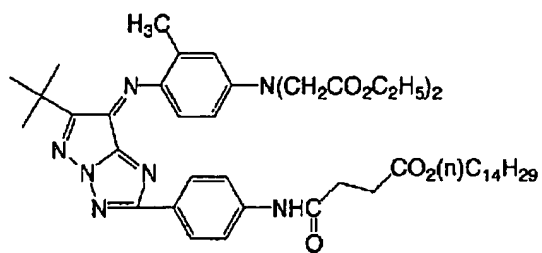
[0070]

[Formula 22]

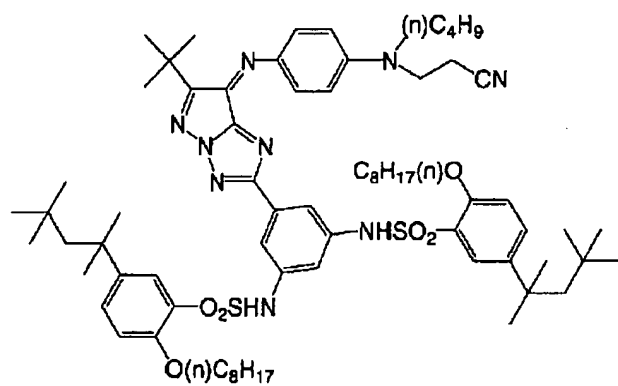
M - 7



M - 8



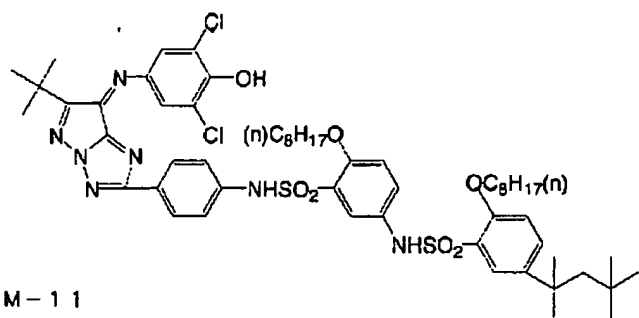
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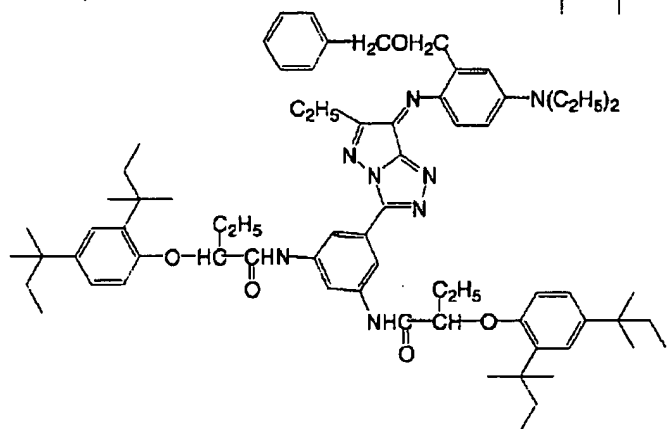
[0071]

[Formula 23]

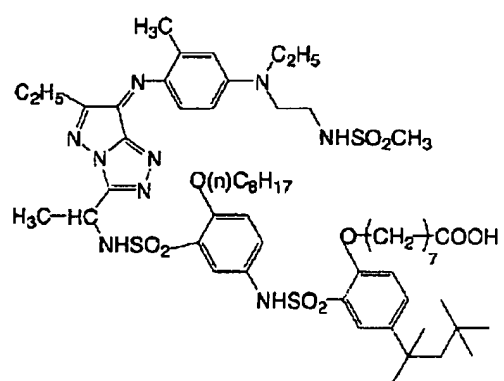
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M-11

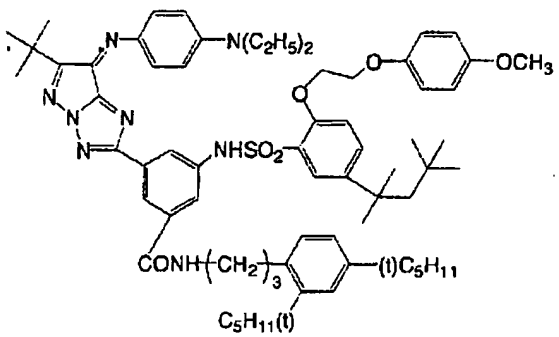


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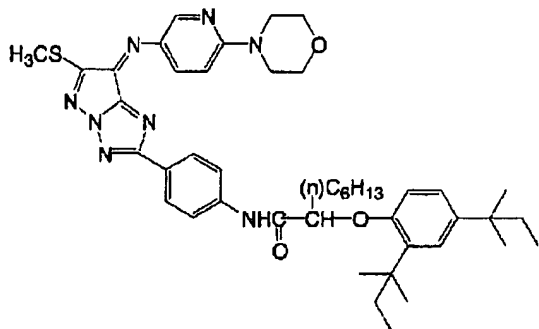


[0072]
[Formula 24]

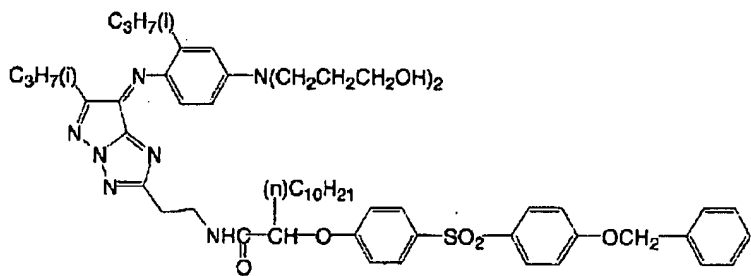
'M-13'



M-14

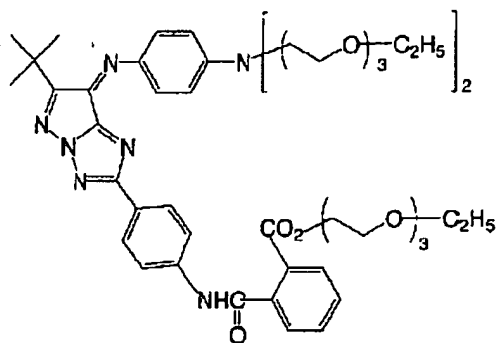


M-15

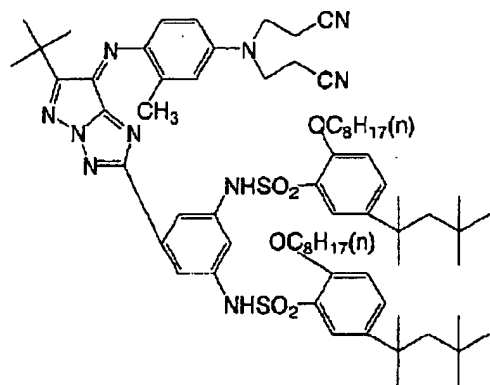


[0073]
[Formula 25]

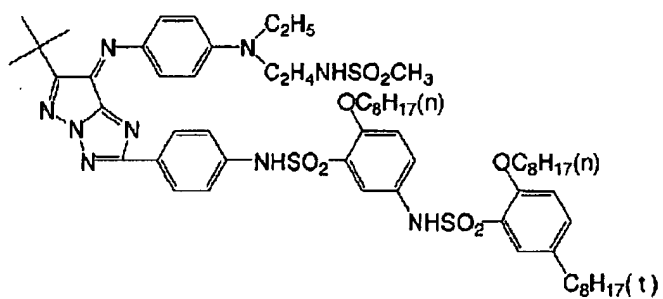
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M-17

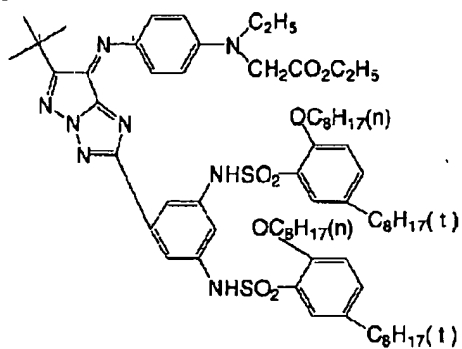


M-18

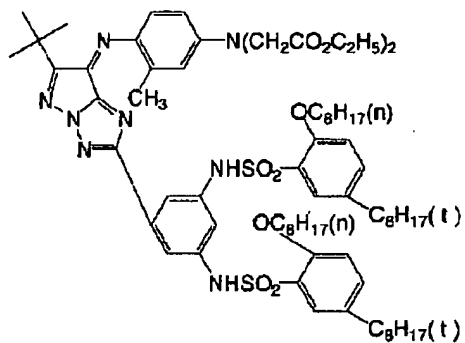


[0074]
[Formula 26]

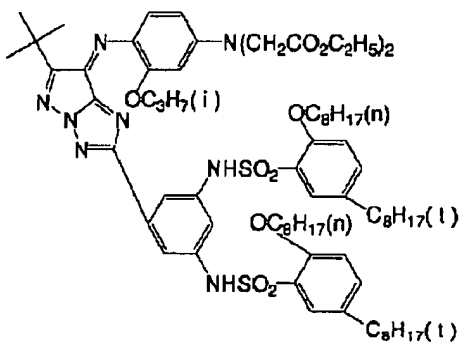
M-19



M-20



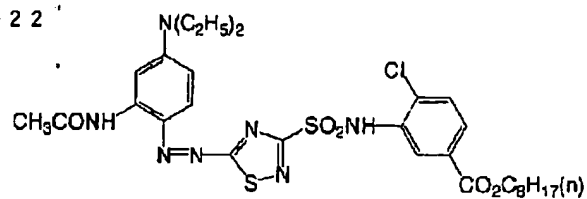
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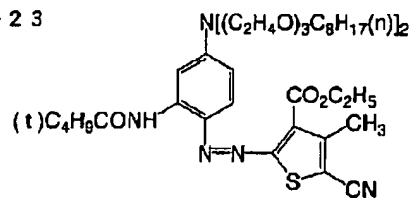
[0075]

[Formula 27]

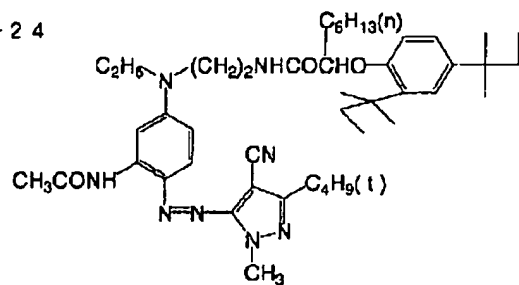
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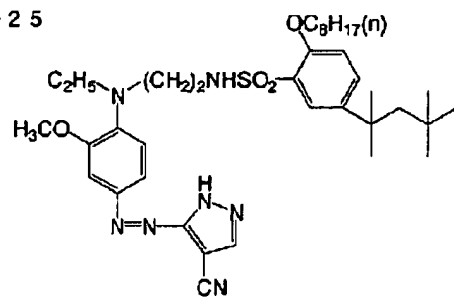
M-23



M-24



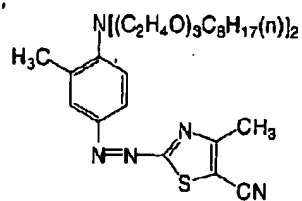
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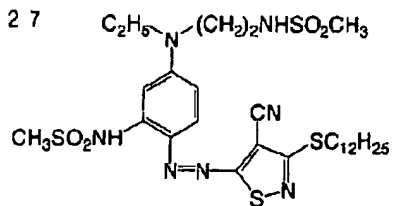
[0076]

[Formula 28]

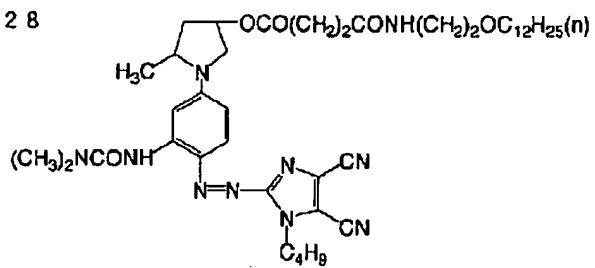
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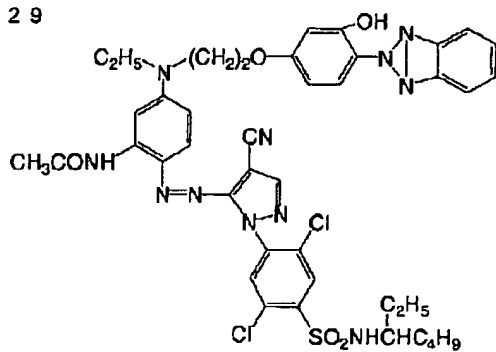
M - 2 7



M - 2 8



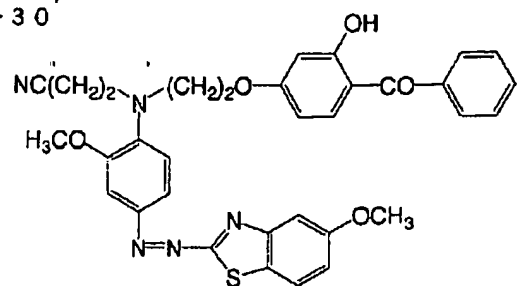
M - 2 9



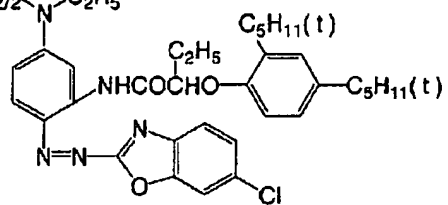
[0077]

[Formula 29]

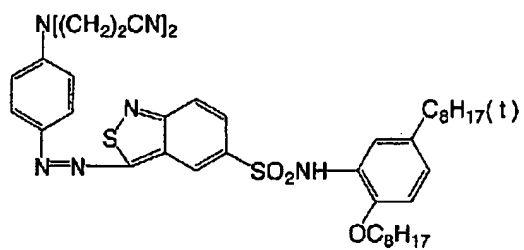
M - 3 0



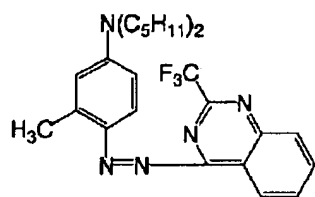
M - 3 1 $\text{CH}_3\text{SO}_2\text{NH}(\text{CH}_2)_2\text{N}-\text{C}_2\text{H}_5$



M - 3 2 $\text{N}[(\text{CH}_2)_2\text{CN}]_2$



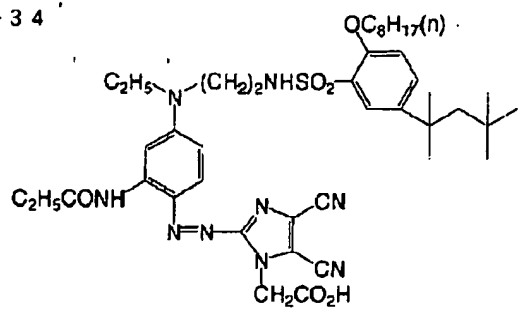
M - 3 3



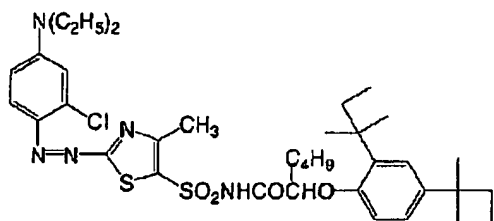
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[Formula 30]

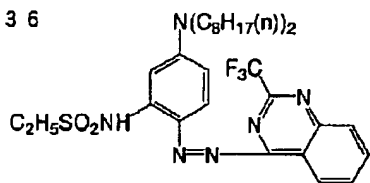
M-34



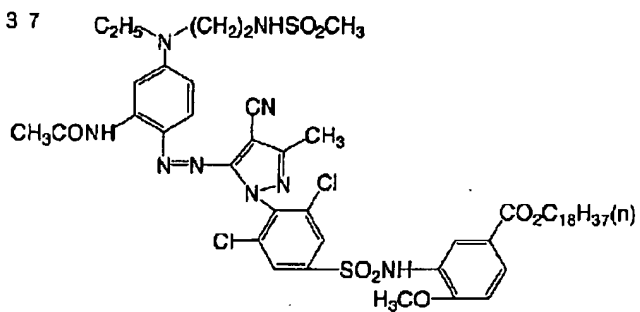
M-35



M-36



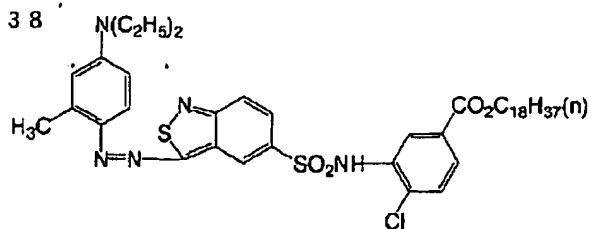
M-37



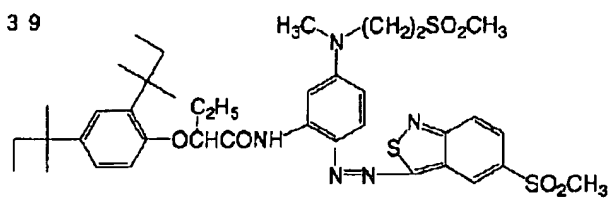
[0079]

[Formula 31]

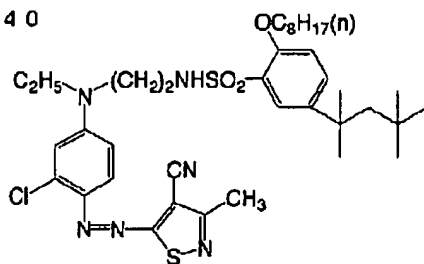
M-38



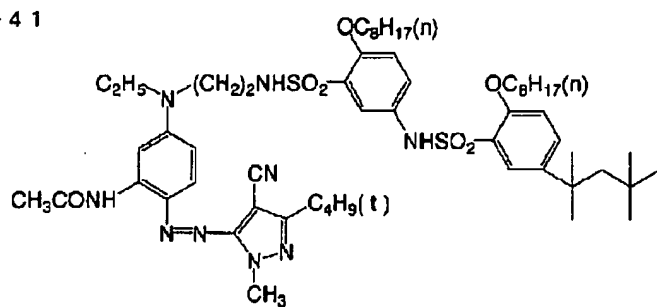
M-39



M-40



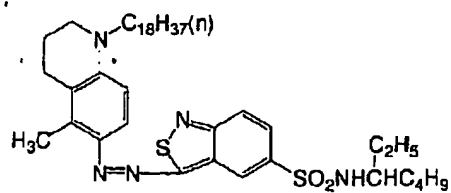
M-41



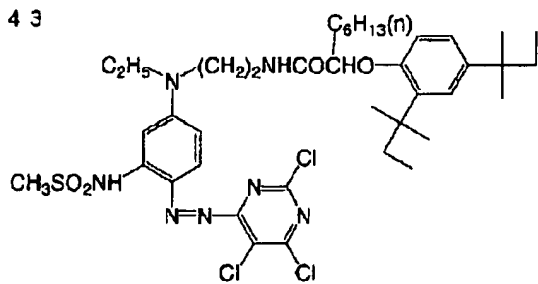
<TXF FR=0001 HE=005 WI=080 LX=0200 LY=1750> [0080]

[Formula 32]

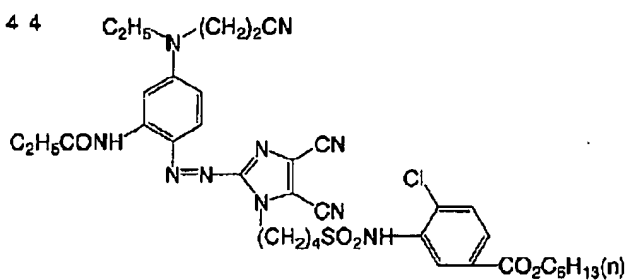
M - 4 2



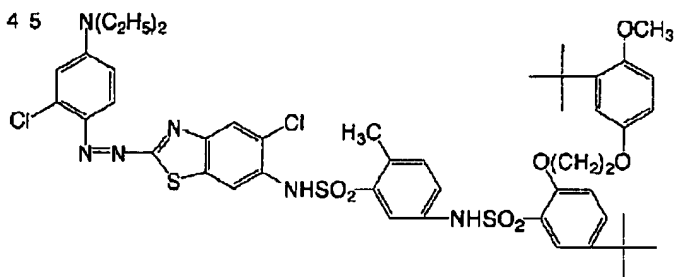
M - 4 3



M - 4 4

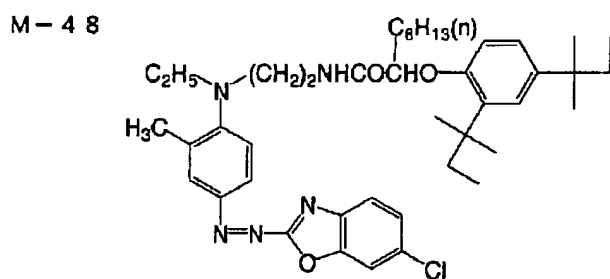
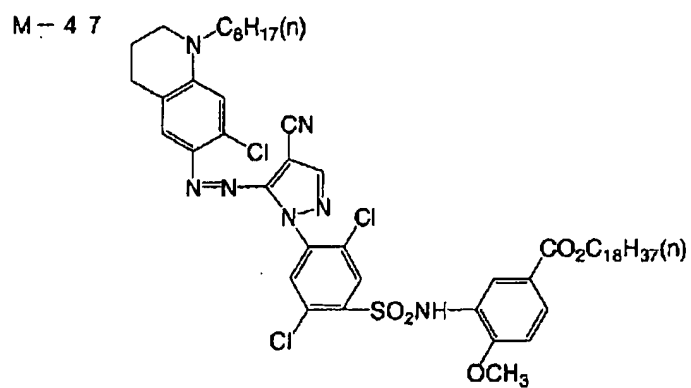
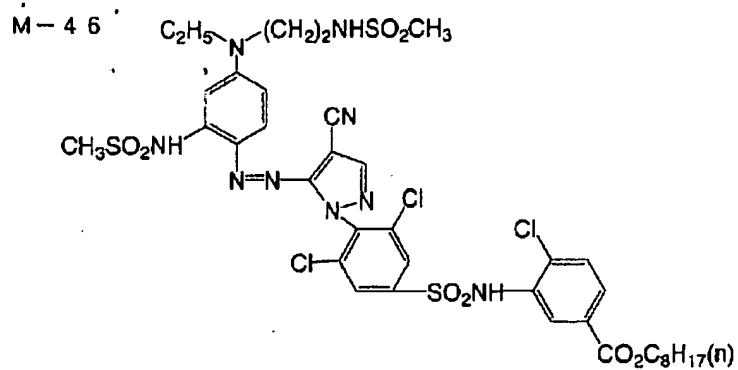


M - 4 5



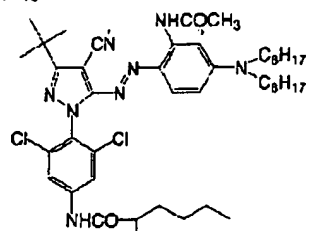
[0081]

[Formula 33]

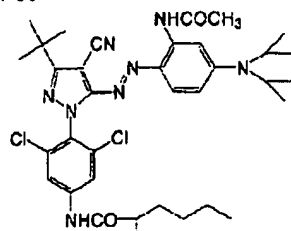


[0082]
[Formula 34]

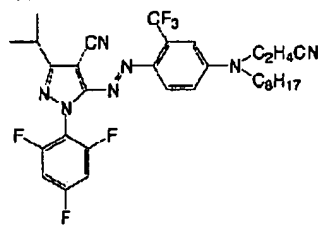
M-49



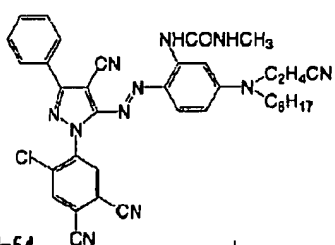
M-50



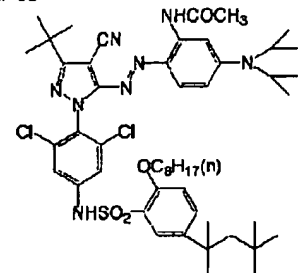
M-51



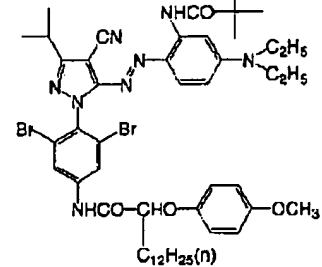
M-52



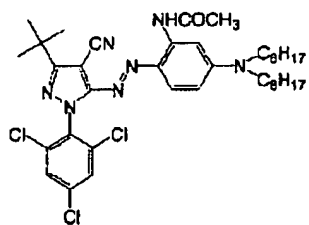
M-53



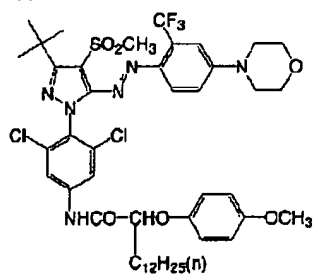
M-54



M-55

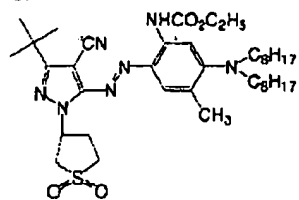


M-56

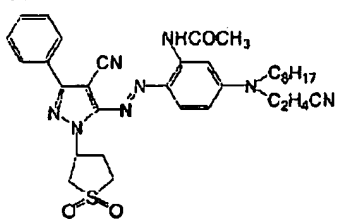


[0083]
[Formula 35]

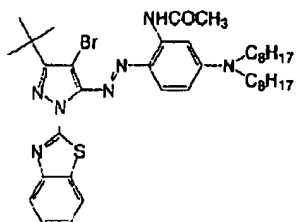
M-57



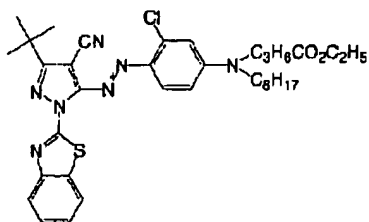
M-58



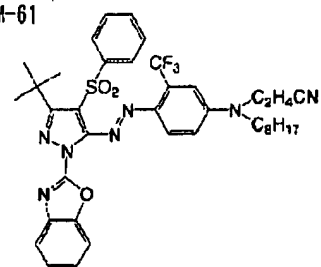
M-59



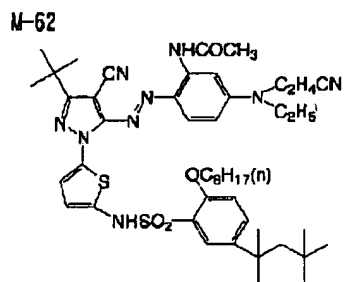
M-60



M-61



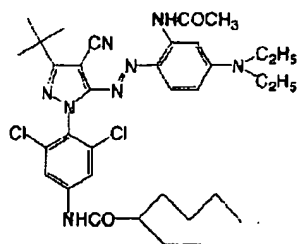
M-62



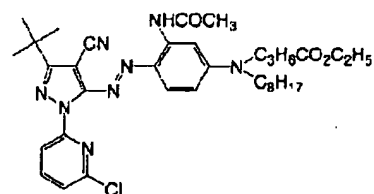
[0084]

[Formula 36]

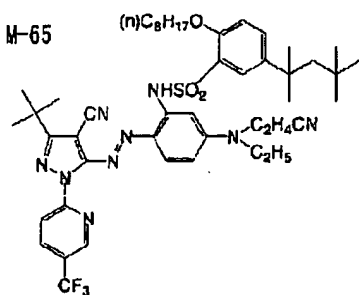
M-63



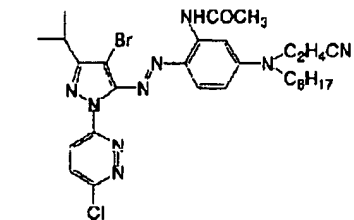
M-64



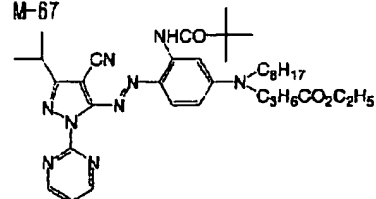
M-65



M-66



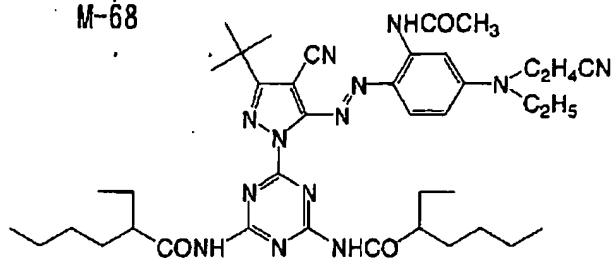
M-67



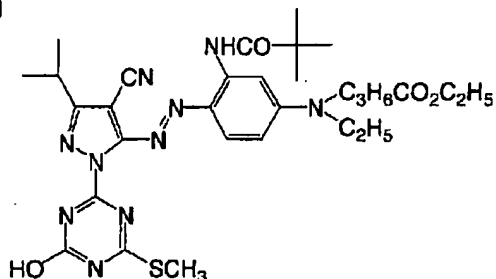
[0085]

[Formula 37]

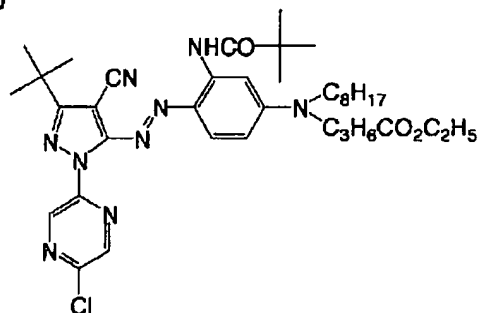
M-68



M-69



M-70



[0086] Although the compound usable to this invention is indicated by Japanese Patent Application No. No. 365187 [11 to] besides said instantiation compound, 11-365190, and the application for patent No. 220649 [2000 to], it is not limited to these.

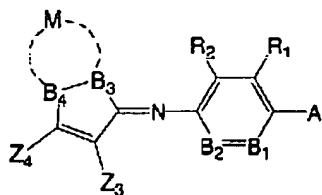
[0087] The coloring matter expressed with the formula (III) of this invention can refer to the approach indicated by an application for patent No. 220649 [2000 to], and JP,55-161856,A, and can compound it. The coloring matter expressed with the formula (IV) of this invention can refer to the approach indicated by JP,4-126772,A, JP,7-94180,B, and the application for patent No. 78491 [2000 to], and can compound it.

[0088] As a cyanogen color, the pyrrolo triazole azomethine color expressed with the following general formula (V) is especially desirable among the colors expressed with said general formula (II).

[0089]

[Formula 38]

一般式 (V)



[0090] In said general formula (V), A, R1, R2, B1, and B-2 are synonymous with said general formula (II), and those desirable range of them is the same as that of said general formula (II). Z3 and Z4 are respectively synonymous with G in said general formula (IV) independently. It may join together mutually and Z3 and Z4 may form a ring structure. M is the atomic group which can form 1, 2, and 4-triazole ring condensed in five membered-rings of said general formula (V), either two atoms B3 in that of the condensation section and B4 are nitrogen atoms, and another side is a carbon atom.

[0091] Furthermore, since absorption is Sharp, that whose Z3 is a with a Hammett substituent constant sigma_p values of 0.30 or more electronic suction nature machine also in the pyrrolo triazole azomethine color expressed with said

general formula (V) is more desirable, what is a with a Hammett substituent constant σ values of 0.45 or more electronic suction nature machine is still more desirable, and especially the thing that is a with a Hammett substituent constant σ values of 0.60 or more electronic suction nature machine is desirable. And the sum of the Hammett substituent constant σ value of Z3 and Z4 presents the hue which was excellent as a cyanogen color, and 0.70 or more things have it. [most desirable]

[0092] In addition, although the pyrrolo triazole azomethine color expressed with said general formula (V) can also be used as a Magenta color by changing a substituent, using as a cyanogen color is desirable.

[0093] Here, Hammett's substituent constant σ value used on these specifications is explained. Although a Hammett rule is a rule of thumb advocated by L.P. Hammett in 1935 in order to discuss quantitatively the effect of the substituent exerted on the reaction or balance of a benzene derivative, as for this, validity is accepted widely today. Although there are σ value and σ_m value in the substituent constant for which the Hammett rule was asked and these values can be found out to many common compendiums, it will be detailed in the 12th edition, 1979 (McGraw-Hill), a volume on J.A. Dean, and "Lange's Handbook of Chemistry" "chemical field" special number, No. 122, 96-103 pages, and 1979 (Nankodo), for example.

[0094] In addition, although each substituent is limited by Hammett's substituent constant σ or is explained in this invention, even if not the semantics that this is limited only to a substituent with the value of reference known which can be found out with the above-mentioned compendium but the value is reference strangeness, when it measures based on a Hammett rule, it cannot be overemphasized that the substituent which will be wrapped within the limits of it is also included. Moreover, although what is not a benzene derivative is contained in said general formula (I) of this invention - the aforementioned general formula (V), regardless of a permutation location, σ value is used as a scale which shows the electronic effectiveness of a substituent. Therefore, in this invention, σ value is used in such semantics.

[0095] A Hammett substituent constant σ value is a cyano group, a nitro group, and an alkyl sulfonyl group (for example, a methane sulfonyl group, an aryl sulfonyl group (for example, benzenesulphonyl radical), etc. are mentioned.) as 0.60 or more electronic suction nature machines.

[0096] In addition to the above, a Hammett σ value is mentioned for an acyl group (for example, acetyl group), an alkoxy carbonyl group (for example, dodecyloxy carbonyl group), an aryloxy carbonyl group (for example, m-chloro phenoxy carbonyl), an alkyl sulfinyl group (for example, n-propyl sulfinyl), an aryl sulfinyl group (for example, phenyl sulfinyl), a sulfamoyl group (for example, N-ethyl sulfamoyl, N, and N-dimethyl sulfamoyl), an alkyl halide radical (for example, TORIFURORO methyl), etc. as 0.45 or more electronic suction nature machines.

[0097] A Hammett substituent constant σ value as 0.30 or more electronic suction nature machines It adds above. An acyloxy radical (for example, acetoxyl), a carbamoyl group (For example, N-ethyl carbamoyl, N, and N-dibutyl carbamoyl), A halogenation alkoxy group (for example, truffle ROROME chill oxy-), a halogenation aryloxy group (For example, pen TAFURORO phenyloxy), a sulfonyloxy radical (for example, methyl sulfonyloxy radical), A halogenation alkylthio group (for example, JIFURORO methylthio), the aryl group by which two or more σ values were permuted with 0.15 or more electronic suction nature machines For example, (2,4-dinitrophenyl and pentachlorophenyl), heterocycle (for example, 2-benzoxazolyl, 2-benzothiazolyl, 1-phenyl 2-benzimidazolyl), etc. are mentioned.

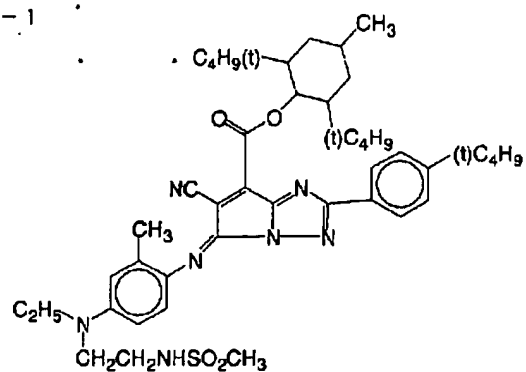
[0098] In addition to the above, σ value is mentioned for a halogen atom etc. as 0.20 or more electronic suction nature machines.

[0099] Although the instantiation compound (C-1-9) of a cyanogen color is shown below among the pyrrolo triazole azomethine colors in this invention, this invention is not limited at all by these.

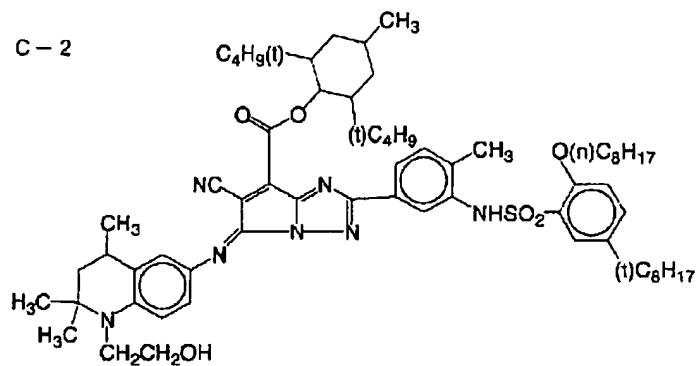
[0100]

[Formula 39]

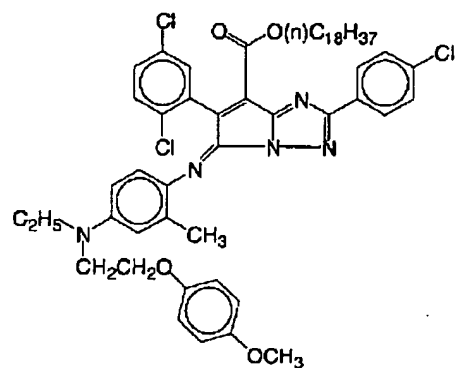
C - 1



C - 2



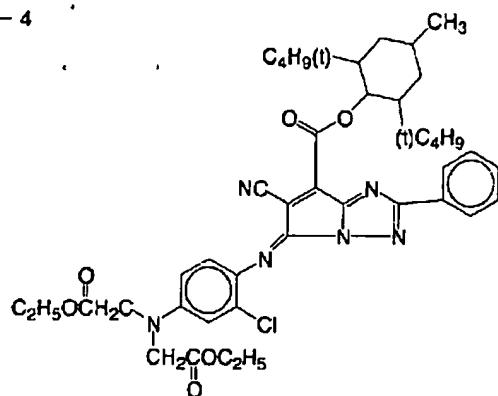
C - 3



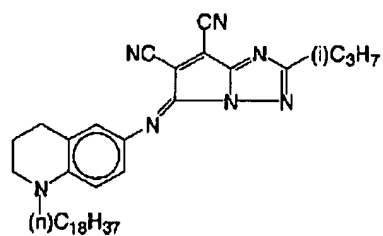
[0101]

[Formula 40]

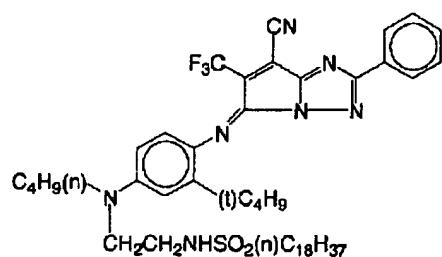
C - 4



C - 5



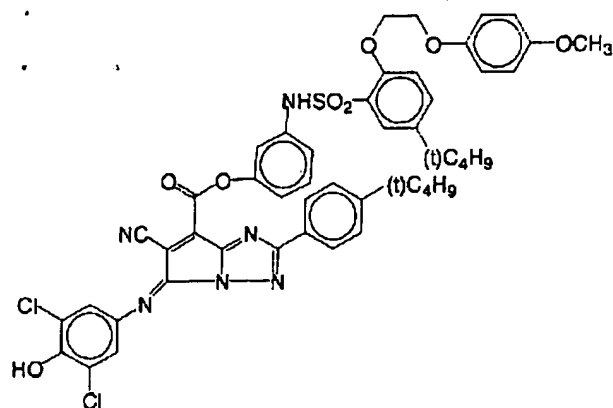
C - 6



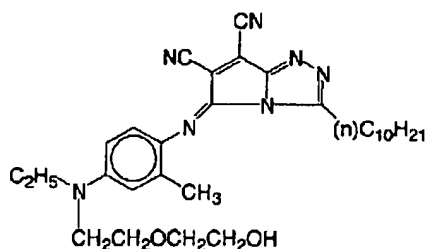
[0102]

[Formula 41]

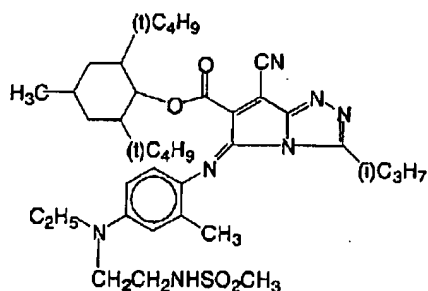
C-7



C-8



C-9



[0103] Although the instantiation compound further indicated by the Japanese-Patent-Application-No. No. 365188 [11 to] specification is mentioned to this invention as an usable color, this invention is not limited to these at all.

[0104] As yellow coloring matter used as hydrophobic coloring matter of this invention, the compound (color) expressed with the following general formula (Y-I) is desirable. [0105]

[Formula 42]

一般式 (Y-I) A-N=N-B

[0106] In said general formula (Y-I), A and B express respectively the heterocycle radical which may be permuted independently. Even if the heterocycle which consisted of five membered-rings or six membered-rings is desirable and is monocycle structure as said heterocycle, you may be the polycyclic structure which two or more rings condensed, and it may be an aromatic heterocycle or you may be non-aromatic heterocycle. As a hetero atom which constitutes said heterocycle, a nitrogen atom, an oxygen atom, and a sulfur atom are desirable. [0107] In said general formula (Y-I), the condensation heterocycle to which a hydrocarbon ring and heterocycle condensed the ring further to 5-pyrazolone, a pyrazole, oxazolone, iso oxazolone, barbituric acid, pyridone, rhodanine, pyrazolidine dione, pyrazolo pyridone, mel drum acids, and such heterocycles is desirable as heterocycle expressed with A. Also in it, 5-pyrazolone, 5-amino pyrazole, pyridone, and pyrazolo azoles are desirable, and 5-amino pyrazole, 2-hydroxy-6-pyridone, and especially pyrazolo triazole are desirable.

[0108] In said general formula (Y-I), as heterocycle expressed with B A pyridine, pyrazine, a pyrimidine, pyridazine, triazine, a quinoline, An isoquinoline, quinazoline, cinnoline, phthalazine, quinoxaline, A pyrrole, Indore, a furan, benzofuran, a thiophene, benzothiophene, A pyrazole, an imidazole, benzimidazole, triazole, oxazole, An isoxazole, benzooxazole, a thiazole, benzothiazole, an iso thiazole, benzoISOCHI azole, thiadiazole, a benzoisoxazole, a pyrrolidine, a piperidine, a piperazine, imidazolidine, thiazoline, etc. are mentioned suitably. Also in it, a pyridine, a quinoline, a thiophene, benzothiophene, A pyrazole, an imidazole, benzimidazole, triazole, oxazole, An isoxazole, benzooxazole, a thiazole, benzothiazole, An iso thiazole, benzoISOCHI azole, thiadiazole, and a benzoisoxazole are

desirable. A quinoline, a thiophene, a pyrazole, a thiazole, benzoxazole, A benzoisoxazole, an iso thiazole, an imidazole, benzothiazole, and thiadiazole are more desirable, and a pyrazole, benzothiazole, benzoxazole, an imidazole, 1 and 2, 4-thiadiazole, 1 and 3, and especially 4-thiadiazole are desirable.

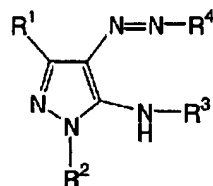
[0109] The substituent permuted by said A and B A halogen atom, an alkyl group, a cycloalkyl radical, An aralkyl radical, an alkenyl radical, an alkynyl group, an aryl group, a heterocycle radical, A cyano group, hydroxyl, a nitro group, an alkoxy group, an aryloxy group, A silyloxy radical, a heterocycle oxy-radical, an acyloxy radical, a carbamoyloxy radical, Alkoxy carbonyloxy group, aryloxy carbonyloxy, The amino group, the acylamino radical, the aminocarbonyl amino group, an alkoxy carbonylamino radical, An aryloxy carbonylamino radical, a sulfamoylamino group, alkyl, and an aryl sulfonylamino radical, A sulfhydryl group, an alkylthio group, an aryl thio radical, a heterocycle thio radical, A sulfamoyl group, alkyl and an aryl sulfinyl group, alkyl, and an aryl sulfonyl group, An acyl group, an aryloxy carbonyl group, an alkoxy carbonyl group, a carbamoyl group, an imide radical, a phosphino radical, a phosphinyl radical, a phosphinyl oxy-radical, the phosphinyl amino group, and a silyl radical are mentioned as an example.

[0110] Also in the color expressed with said general formula (Y-I), the following general formula (Y-II), (Y-III), and (Y-IV) the color expressed are more desirable.

[0111]

[Formula 43]

一般式 (Y-II)

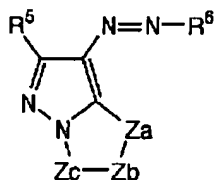


[0112] In said general formula (Y-II), R1 and R3 express a hydrogen atom, a cyano group, an alkyl group, a cycloalkyl radical, an aralkyl radical, an alkoxy group, an alkylthio group, an aryl thio radical, an aryl group, or an ionicity hydrophilic radical. R2 expresses a hydrogen atom, an alkyl group, a cycloalkyl radical, an aralkyl radical, a carbamoyl group, an acyl group, an aryl group, or a heterocycle radical. R4 expresses a heterocycle radical.

[0113]

[Formula 44]

一般式 (Y-III)

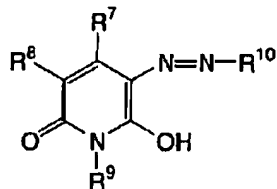


[0114] In said general formula (Y-III), R5 expresses a hydrogen atom, a cyano group, an alkyl group, a cycloalkyl radical, an aralkyl radical, an alkoxy group, an alkylthio group, an aryl thio radical, an aryl group, or an ionicity hydrophilic radical. Za expresses -N=, -NH-, or C(R11) =, Zb and Zc express respectively independently -N= or C (R11) =, and said R11 expresses a hydrogen atom or a nonmetal substituent. R6 expresses a heterocycle radical.

[0115]

[Formula 45]

一般式 (Y-IV)



[0116] In said general formula (Y-IV), R7 and R9 express respectively independently a hydrogen atom, a cyano group, an alkyl group, a cycloalkyl radical, an aralkyl radical, an aryl group, an alkylthio group, an aryl thio radical, an alkoxy carbonyl group, a carbamoyl group, or an ionicity hydrophilic radical. R8 expresses a hydrogen atom, a halogen atom,

an alkyl group, an alkoxy group, an aryl group, an aryloxy group, a cyano group, the acylamino radical, a sulfonylamino radical, an alkoxycarbonylamino radical, an ureido radical, an alkylthio group, an aryl thio radical, an alkoxy carbonyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, an acyl group, an alkylamino radical, an arylamino radical, a hydroxy group, or an ionicity hydrophilic radical. R10 expresses a heterocycle radical.

[0117] The substituent which said general formula (Y-II), (Y-III), and (Y-IV) R1, R2, R3, R5, R7, R8 and R9 that can be set express is explained in full detail below.

[0118] The alkyl group which has a substituent, and a non-permuted alkyl group are contained in the alkyl group which R1, R2, R3, R5, R7, R8, and R9 express. As said alkyl group, the alkyl group of 1-20 has a desirable carbon atomic number, and hydroxyl, an alkoxy group, a cyano group, a halogen atom, and an ionicity hydrophilic radical are mentioned as an example of said substituent. As said alkyl group, methyl, ethyl, butyl, isopropyl, t-butyl, hydroxyethyl, methoxy ethyl, cyano ethyl, trifluoromethyl, 3-sulfopropyl, and 4-sulfo butyl are mentioned suitably, for example.

[0119] The cycloalkyl radical which has a substituent, and a non-permuted cycloalkyl radical are contained in the cycloalkyl radical which R1, R2, R3, R5, R7, R8, and R9 express. As said cycloalkyl radical, the cycloalkyl radical of 5-12 has a desirable carbon atomic number, and an ionicity hydrophilic radical is mentioned as an example of said substituent. As said cycloalkyl radical, cyclohexyl is mentioned suitably, for example.

[0120] The aralkyl radical which has a substituent, and a non-permuted aralkyl radical are contained in the aralkyl radical which R1, R2, R3, R5, R7, R8, and R9 express. As said aralkyl radical, the aralkyl radical of 7-20 has a desirable carbon atomic number, and an ionicity hydrophilic radical is mentioned as the example of said substituent. As said aralkyl radical, benzyl and 2-phenethyl are mentioned suitably.

[0121] The aryl group which has a substituent, and a non-permuted aryl group are contained in the aryl group which R1, R2, R3, R5, R7, and R9 express. As said aryl group, the aryl group of 6-20 has a desirable carbon atomic number, and an alkyl group, an alkoxy group, a halogen atom, an alkylamino radical, and an ionicity hydrophilic radical are mentioned as the example of said substituent. As an example of said aryl group, phenyl, p-tolyl, p-methoxyphenyl, o-chlorophenyl, and m-(3-sulfopropyl amino) phenyl are mentioned suitably.

[0122] The alkylthio group which has a substituent, and a non-permuted alkylthio group are contained in the alkylthio group which R1, R2, R3, R5, R7, R8, and R9 express. As said alkylthio group, the alkylthio group of 1-20 has a desirable carbon atomic number, and an ionicity hydrophilic radical is mentioned as the example of said substituent. As said alkylthio group, a methylthio and ethyl thio are mentioned suitably.

[0123] The aryl thio radical which has a substituent, and a non-permuted aryl thio radical are contained in the aryl thio radical which R1, R2, R3, R5, R7, R8, and R9 express. As said aryl thio radical, the aryl thio radical of 6-20 has a desirable carbon atomic number, and an alkyl group and an ionicity hydrophilic radical are mentioned as an example of said substituent. As said aryl thio radical, a phenylthio radical and p-tolyl thio are mentioned suitably, for example.

[0124] The heterocycle radical expressed with R2 has the desirable heterocycle of 5 members or 6 members, and they may be condensing the ring further. As a hetero atom which constitutes heterocycle, a nitrogen atom, a sulfur atom, and an oxygen atom are desirable. Moreover, it may be an aromatic heterocycle or you may be non-aromatic heterocycle. Said heterocycle may be permuted further and the same thing as the substituent of the below-mentioned aryl group is suitably mentioned as an example of this substituent. As desirable heterocycle, the nitrogen-containing aromatic heterocycle of 6 members is mentioned, and triazine, a pyrimidine, and especially phthalazine are desirable also in it.

[0125] As a halogen atom which R8 expresses, a fluorine atom, a chlorine atom, and a bromine atom are mentioned suitably. The alkoxy group which has a substituent, and a non-permuted alkoxy group are contained in the alkoxy group which R1, R3, R5, and R8 express. As said alkoxy group, the alkoxy group of 1-20 has a desirable carbon atomic number, and hydroxyl and an ionicity hydrophilic radical are contained as an example of said substituent. As said alkoxy group, methoxy and ethoxy ** isopropoxy, methoxyethoxy, and hydroxy ethoxy ** and 3-carboxy propoxy are mentioned suitably, for example.

[0126] The aryloxy group which has a substituent, and a non-permuted aryloxy group are contained in the aryloxy group which R8 expresses. As said aryloxy group, the aryloxy group of 6-20 has a desirable carbon atomic number, and an alkoxy group and an ionicity hydrophilic radical are contained in the example of said substituent. As said aryloxy group, phenoxy, p-methoxy phenoxy, and o-methoxy phenoxy are mentioned suitably, for example. The acylamino radical which has a substituent, and the non-permuted acylamino radical are contained in the acylamino radical which R8 expresses. As said acylamino radical, the acylamino radical of 2-20 has a desirable carbon atomic number, and an ionicity hydrophilic radical is contained in the example of said substituent. As said acylamino radical, an acetamide, propione amide, benzamide and 3, and 5-disulfo benzamide is mentioned suitably, for example.

[0127] The sulfonylamino radical which has a substituent, and a non-permuted sulfonylamino radical are contained in the sulfonylamino radical which R8 expresses. As said sulfonylamino radical, the sulfonylamino radical of 1-20 has a desirable carbon atomic number. As said sulfonylamino radical, methylsulfonylamino and ethyl sulfonylamino are mentioned suitably, for example.

[0128] The alkoxycarbonylamino radical which has a substituent, and a non-permuted alkoxycarbonylamino radical are contained in the alkoxycarbonylamino radical which R8 expresses. As said alkoxycarbonylamino radical, the alkoxycarbonylamino radical of 2-20 has a desirable carbon atomic number, and an ionicity hydrophilic radical is contained in the example of said substituent. As said alkoxycarbonylamino radical, ethoxycarbonylamino is mentioned suitably.

[0129] The ureido radical which has a substituent, and a non-permuted ureido radical are contained in the ureido radical which R8 expresses. As said ureido radical, the ureido radical of 1-20 has a desirable carbon atomic number, and an alkyl group and an aryl group are contained as an example of said substituent. As said ureido radical, 3-methyl ureido, 3, and 3-dimethyl ureido and 3-phenyl ureido are mentioned suitably, for example.

[0130] The alkoxy carbonyl group which has a substituent, and a non-permuted alkoxy carbonyl group are contained in the alkoxy carbonyl group which R7, R8, and R9 express. As said alkoxy carbonyl group, the alkoxy carbonyl group of 2-20 has a desirable carbon atomic number, and an ionicity hydrophilic radical is contained in the example of said substituent. As said alkoxy carbonyl group, methoxycarbonyl and ethoxycarbonyl are mentioned suitably, for example.

[0131] The carbamoyl group which has a substituent, and a non-permuted carbamoyl group are contained in the carbamoyl group which R2, R7, R8, and R9 express. An alkyl group is contained in the example of said substituent. As said carbamoyl group, a methyl carbamoyl group and a dimethyl carbamoyl group are mentioned suitably, for example. The sulfamoyl group which has a substituent, and a non-permuted sulfamoyl group are contained in the sulfamoyl group which R8 expresses. An alkyl group is contained in the example of said substituent. As said sulfamoyl group, a dimethyl sulfamoyl group and a G (2-hydroxyethyl) sulfamoyl group are mentioned suitably, for example.

[0132] As a sulfonyl group which R8 expresses, a methane sulfonyl and a phenyl sulfonyl are mentioned suitably, for example. The acyl group which has a substituent, and a non-permuted acyl group are contained in the acyl group which R2 and R8 express. As said acyl group, the acyl group of 1-20 has a desirable carbon atomic number, and an ionicity hydrophilic radical is contained in the example of said substituent. As said acyl group, acetyl and benzoyl are mentioned suitably.

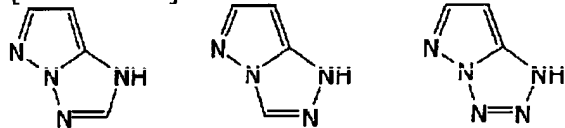
[0133] The amino group which has a substituent, and the non-permuted amino group are contained in the amino group which R8 expresses. An alkyl group, an aryl group, and a heterocycle radical are contained in the example of a substituent. As said amino group, methylamino, diethylamino, ANIRINO, and 2-chloroanilino are mentioned suitably.

[0134] The heterocycle radical expressed with R4, R6, and R10 is the same as the heterocycle radical which is expressed with B of said general formula (Y-I) and which may be permuted, and a desirable example, a still more desirable example, and the especially desirable example of it are the same as that of the above. As a substituent, the alkyl group, the aryl group, the alkyl or the aryl thio radical, the halogen atom, a cyano group, a sulfamoyl group, a sulfone amino group, a carbamoyl group, the acylamino radical, etc. of 1-12 are mentioned, and, as for said alkyl group, aryl group, etc., the ionicity hydrophilic radical and the carbon atomic number may have the substituent further.

[0135] In said general formula (Y-III), Za expresses -N=, -NH-, or C(R11) =. Zb and Zc express respectively independently -N= or C(R11) =. R11 expresses a hydrogen atom or a nonmetal substituent. As a nonmetal substituent which R11 expresses, a cyano group, a cycloalkyl radical, an aralkyl radical, an aryl group, an alkylthio group, an aryl thio radical, or an ionicity hydrophilic radical is desirable. Each of said substituent is synonymous with each substituent which R1 expresses, and its same is said of a desirable example. The example of a frame of the heterocycle which consists of two membered-rings [five] included in said general formula (Y-III) is shown below.

[0136]

[Formula 46]

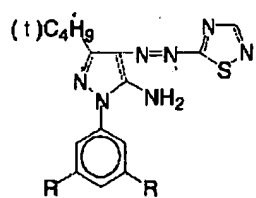


[0137] Each substituent explained above can mention the substituent which may be permuted by the heterocycles A and B of said general formula (Y-I) as an example of the substituent in the case of having the substituent further.

[0138] Although the example (Y-101 to Y-155) of a color expressed with said general formula (Y-I) below is shown, the color used for this invention is not limited to the following example. These compounds refer to each official report of JP,2-24191,A and JP,2001-279145,A, and can compound it.

[0139]

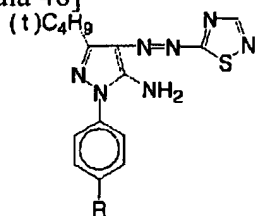
[Formula 47]



色素	R
Y-101	$\text{CON}(\text{C}_2\text{H}_5)_2$
Y-102	$\text{CON}(\text{C}_4\text{H}_9)_2$
Y-103	$\text{CON}(\text{C}_6\text{H}_{13})_2$
Y-104	COOC_4H_9
Y-105	$\text{COOC}_8\text{H}_{17}$
Y-106	COC_4H_9
Y-107	CONHC_4H_9
Y-108	$\text{CONHC}_8\text{H}_{17}$

[0140]

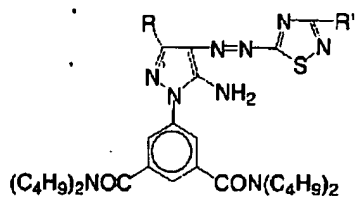
[Formula 48]



色素	R
Y-109	COOC_4H_9
Y-110	CONHC_4H_9
Y-111	$\text{CON}(\text{C}_4\text{H}_9)_2$
Y-112	$\text{SO}_2\text{NHC}_8\text{H}_{17}$
Y-113	$\text{SO}_2\text{N}(\text{C}_4\text{H}_9)_2$
Y-114	$\text{NHCOC}_8\text{H}_{17}$
Y-115	$\text{NHSO}_2\text{C}_8\text{H}_{17}$
Y-116	C_4H_9
Y-117	OC_8H_{17}
Y-118	$\text{COOC}_{12}\text{H}_{25}$
Y-119	NHCOCHO
Y-120	NHSO_2

[0141]

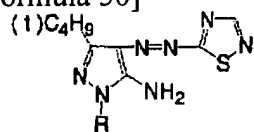
[Formula 49]



色素	R	R'
Y-121	CH ₃	H
Y-122	Ph	H
Y-123	OC ₂ H ₅	H
Y-124	C ₄ H ₉ (t)	SCH ₃
Y-125	C ₄ H ₉ (t)	Ph
Y-126	C ₄ H ₉ (t)	CH ₃
Y-127	C ₄ H ₉ (t)	SC ₈ H ₁₇

[0142]

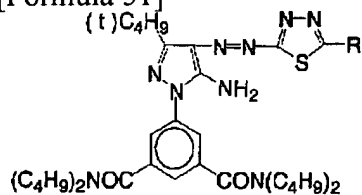
[Formula 50]



色素	R
Y-128	CH ₂ Ph
Y-129	C ₄ H ₉
Y-130	C ₈ H ₁₇
Y-131	CONH ₂

[0143]

[Formula 51]

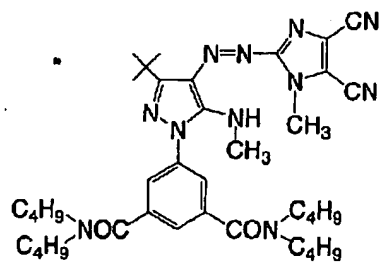


色素	R
Y-132	H
Y-133	CH ₃
Y-134	Ph
Y-135	SCH ₃

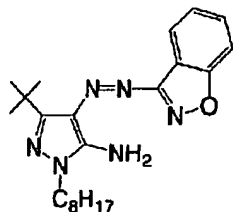
[0144]

[Formula 52]

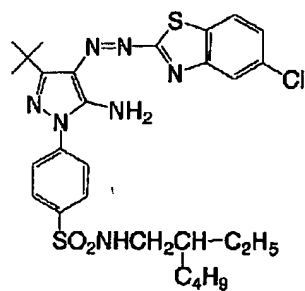
Y-136



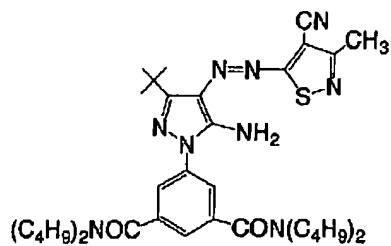
Y-137



Y-138

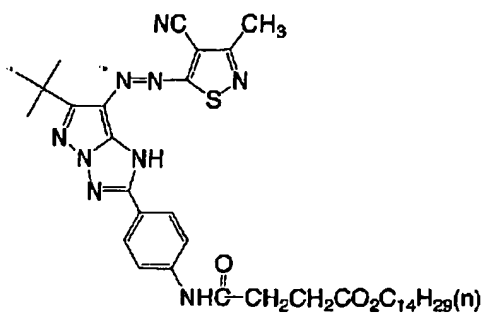


Y-139

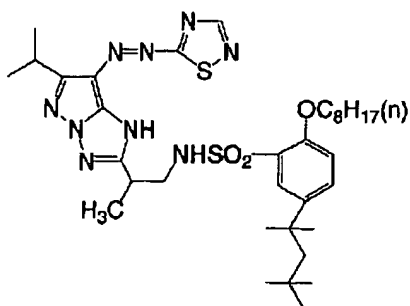


[0145]
[Formula 53]

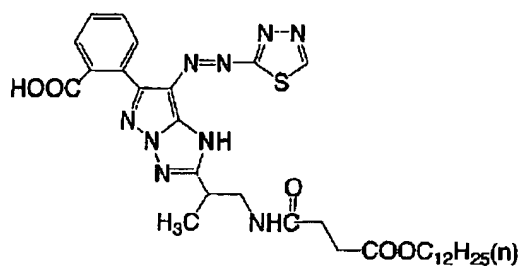
Y-140



Y-141



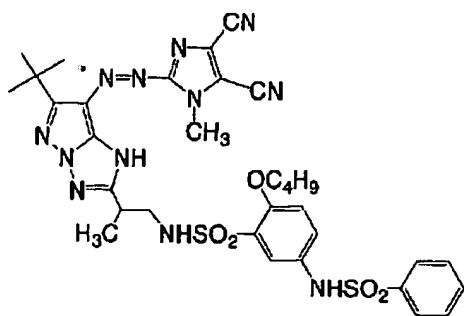
Y-142



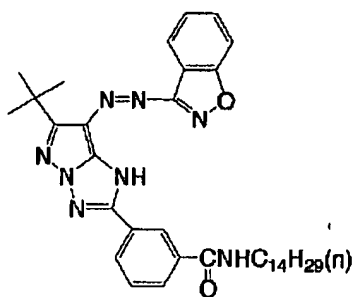
[0146]

[Formula 54]

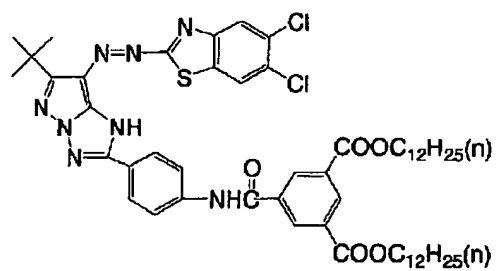
Y-143



Y-144

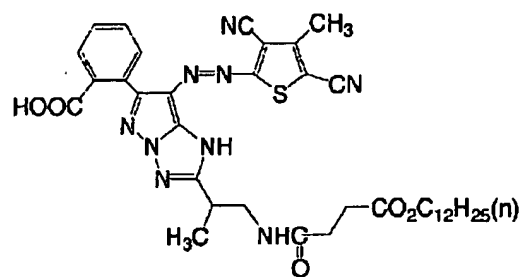


Y-145

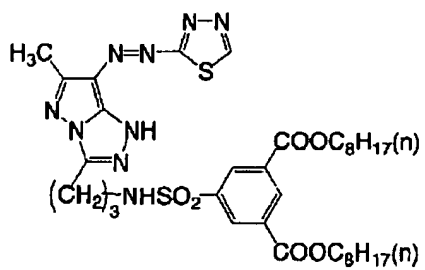


[0147]
[Formula 55]

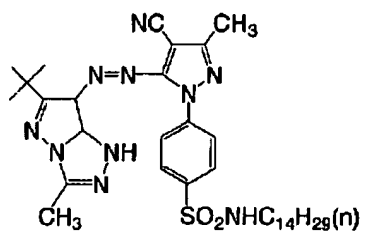
Y-146



Y-147

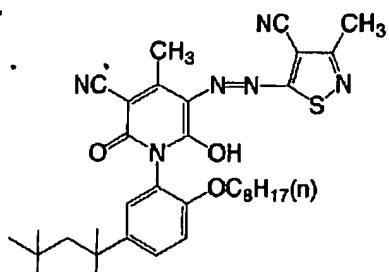


Y-148

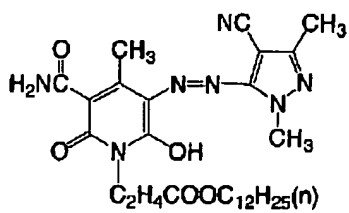


[0148]
[Formula 56]

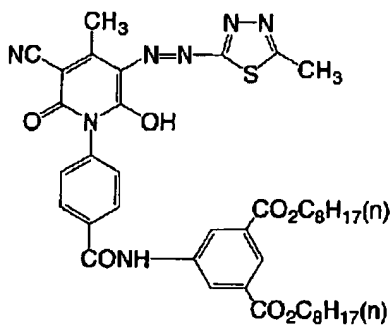
Y-149



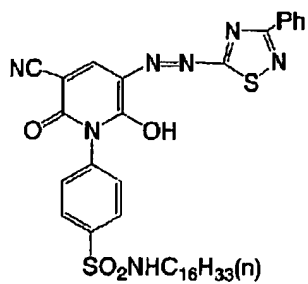
Y-150



Y-151



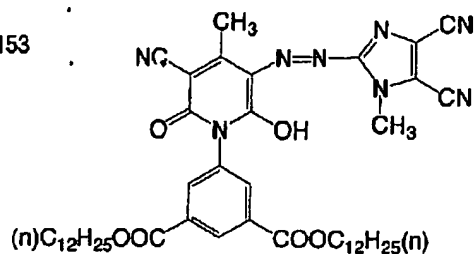
Y-152



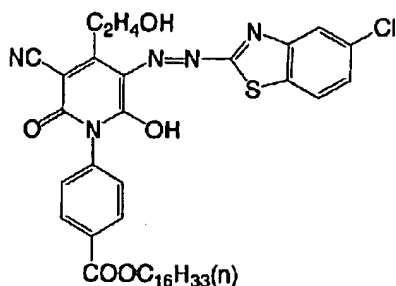
[0149]

[Formula 57]

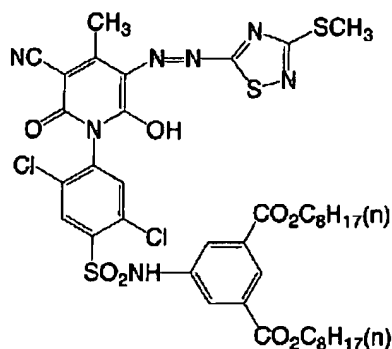
Y-153



Y-154



Y-155

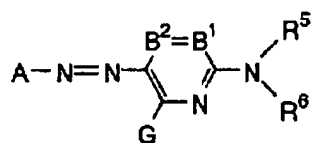


[0150] Furthermore, as oil solubility coloring matter suitably used as hydrophobic coloring matter of this invention, the compound ("azo dye" may be called hereafter) expressed with the following general formula (M-I) is desirable. The compound expressed with the general formula (M-I) of this invention below is explained.

[0151]

[Formula 58]

一般式 (M-I)



[0152] In said general formula (M-I), A expresses the residue of 5 member heterocycle diazo component A-NH2. B1 expresses =CR1-, B-2 expresses -CR2=, or either expresses a nitrogen atom and, as for B1 and B-2, another side expresses =CR1- or -CR2=. R5 and R6 express a hydrogen atom, an aliphatic series radical, an aromatic series radical, a heterocycle radical, an acyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a carbamoyl group, an alkyl sulfonyl group, an aryl sulfonyl group, or a sulfamoyl group independently respectively. Each radical may have the substituent further. G, R1, and R2 become independent respectively. A hydrogen atom, a halogen atom, an aliphatic series radical, An aromatic series radical, a heterocycle radical, a cyano group, a carboxyl group, a carbamoyl group, An alkoxy carbonyl group, an aryloxy carbonyl group, an acyl group, A hydroxy group, an alkoxy group, an aryloxy group, a silyloxy radical, An acyloxy radical, a carbamoyloxy radical, a heterocycle oxy-radical, alkoxy carbonyloxy group, The amino group permuted by aryloxy carbonyloxy group, the alkyl group, the aryl group, or the heterocycle radical, The acylamino radical, an ureido radical, a sulfamoylamino group, an alkoxy carbonylamino radical, An aryloxy carbonylamino radical, an alkyl aryl sulfonylamino radical, An aryl sulfonylamino radical, an aryloxy carbonylamino radical, A nitro group, an alkylthio group, an aryl thio radical, an alkyl sulfonyl group, an aryl

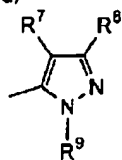
sulfonyl group, an alkyl sulfinyl group, an aryl sulfinyl group, a sulfamoyl group, a sulfonic group, or a heterocycle thio radical is expressed. Each radical may be permuted further. Moreover, R1, R5, or R5 and R6 may join together, and five to 6 membered-ring may be formed.

[0153] The compound expressed with said general formula (M-I) of this invention is explained to a detail. In said general formula (M-I), A expresses the residue of 5 member heterocycle diazo component A-NH2. N, O, and S can be mentioned as an example of the hetero atom of this 5 member heterocycle. ***** is nitrogen-containing 5 member heterocycle, and an aliphatic series ring, an aromatic series ring, or other heterocycles may condense it in heterocycle. As an example of the desirable heterocycle of A, a pyrazole ring, an imidazole ring, a thiazole ring, an iso thiazole ring, a thiadiazole ring, a benzothiazole ring, a benzoxazole ring, and a benzoISOCHI azole ring can be mentioned. Each heterocycle radical may have the substituent further. Especially, the pyrazole ring expressed with (M-f) from the following general formula (M-a), an imidazole ring, an iso thiazole ring, a thiadiazole ring, and a benzothiazole ring are desirable.

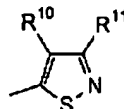
[0154]

[Formula 59]

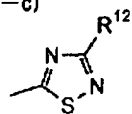
(M-a)



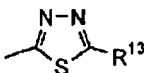
(M-b)



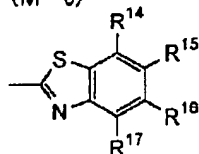
(M-c)



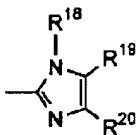
(M-d)



(M-e)



(M-f)



[0155] R7-R20 of said general formula (M-a) - (M-f) express the same substituent as the substituents G, R1, and R2 explained later. A general formula (M-a) and (M-b) the pyrazole ring expressed, and an iso thiazole ring are desirable among said general formula (M-a) - (M-f), and the pyrazole ring expressed with a general formula (M-a) is the most desirable. Although B1 expresses =CR1-, B-2 expresses -CR2=, or either expresses a nitrogen atom and another side expresses =CR1- or -CR2=, as for B1 and B-2, what B1 expresses =CR1- and B-2 expresses -CR2= to is more desirable. R5 and R6 may express a hydrogen atom, an aliphatic series radical, an aromatic series radical, a heterocycle radical, an acyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a carbamoyl group, an alkyl sulfonyl group, an aryl sulfonyl group, or a sulfamoyl group independently respectively, and each radical may have the substituent further. A hydrogen atom, an aliphatic series radical, an aromatic series radical, a heterocycle radical, an acyl group, an alkyl sulfonyl group, and an aryl sulfonyl group can be mentioned to the desirable substituent expressed with R5 and R6. They are a hydrogen atom, an aromatic series radical, a heterocycle radical, an acyl group, an alkyl sulfonyl group, or an aryl sulfonyl group still more preferably. They are a hydrogen atom, an aryl group, or a heterocycle radical most preferably. Each radical may have the substituent further. However, R5 and R6 are not hydrogen atoms at coincidence.

[0156] Respectively G, R1, and R2 independently A hydrogen atom, a halogen atom, an aliphatic series radical, An aromatic series radical, a heterocycle radical, a cyano group, a carboxyl group, a carbamoyl group, An alkoxy carbonyl group, an aryloxy carbonyl group, an acyl group, A hydroxy group, an alkoxy group, an aryloxy group, a silyloxy radical, An acyloxy radical, a carbamoyloxy radical, a heterocycle oxy-radical, alkoxy carbonyloxy group, The amino group permuted by aryloxy carbonyloxy group, the alkyl group, the aryl group, or the heterocycle radical, The acylamino radical, an ureido radical, a sulfamoylamino group, an alkoxy carbonylamino radical, An aryloxy carbonylamino radical, an alkyl sulfonylamino radical, An aryl sulfonylamino radical, a nitro group, an alkylthio group, an aryl thio radical, A heterocycle thio radical, an alkyl sulfonyl group, an aryl sulfonyl group, an alkyl sulfinyl group, an aryl sulfinyl group, a sulfamoyl group, or a sulfonic group is expressed, and each radical may be permuted further.

[0157] As a desirable substituent expressed with G, a hydrogen atom, a halogen atom, an aliphatic series radical, An

aromatic series radical, a hydroxy group, an alkoxy group, an aryloxy group, an acyloxy radical, The amino group permuted by the heterocycle oxy-radical, the alkyl group, the aryl group, or the heterocycle radical, The acylamino radical, an ureido radical, a sulfamoylamino group, an alkoxycarbonylamino radical, An aryloxy carbonylamine radical, an alkylthio group, an aryl thio radical, and a heterocycle thio radical are mentioned. More preferably A hydrogen atom, a halogen atom, an alkyl group, a hydroxy group, an alkoxy group, It is the amino group permuted by an aryloxy group, the acyloxy radical, the alkyl group, the aryl group, or the heterocycle radical, or the acylamino radical, and a hydrogen atom, an arylamino radical, and an amide group are the most desirable especially. Each radical may have the substituent further.

[0158] As a desirable substituent expressed with R1 and R2, a hydrogen atom, an alkyl group, an alkoxy carbonyl group, a carboxyl group, a carbamoyl group, and a cyano group can be mentioned. Each radical may have the substituent further. R1, R5, or R5 and R6 may join together, and five to 6 membered-ring may be formed. As a substituent in case each substituent expressed with A, R1, R2, R5, R6, and G has a substituent further, the substituent mentioned by said G, R1, and R2 can be mentioned.

[0159] Hereafter, the substituent expressed with G, R1, and R2 is explained in detail. As a halogen atom, a fluorine atom, a chlorine atom, and a bromine atom are mentioned. An aliphatic series radical means an alkyl group, a permutation alkyl group, an alkenyl radical, a permutation alkenyl radical, an alkynyl group, a permutation alkynyl group, an aralkyl radical, and a permutation aralkyl radical. The aliphatic series radical may have branching and may form the ring. As for the carbon atomic number of an aliphatic series radical, it is desirable that it is 1-20, and it is still more desirable that it is 1-16. As for the aryl parts of an aralkyl radical and a permutation aralkyl radical, it is desirable that they are phenyl or naphthyl, and especially its phenyl is desirable. As an example of an aliphatic series radical, a methyl group, an ethyl group, butyl, an isopropyl group, t-butyl, a hydroxyethyl radical, a methoxy ethyl group, a cyano ethyl group, a trifluoromethyl radical, 3-sulfopropyl radical, 4-sulfo butyl, a cyclohexyl radical, benzyl, 2-phenethyl radical, a vinyl group, and an allyl group can be mentioned.

[0160] In this specification, an aromatic series radical means an aryl group and a permutation aryl group. As for an aryl group, it is desirable that they are a phenyl group or a naphthyl group, and especially its phenyl group is desirable. As for the carbon atomic number of an aromatic series radical, it is desirable that it is 6-20, and 6-16 are still more desirable. As an example of an aromatic series radical, a phenyl group, p-tolyl group, p-methoxyphenyl radical, o-chlorophenyl radical, and m-(3-sulfopropyl amino) phenyl group are contained. The heterocycle radical which has a substituent, and a non-permuted heterocycle radical are contained in a heterocycle radical. An aliphatic series ring, an aromatic series ring, or other heterocycles may condense in heterocycle. As a heterocycle radical, the heterocycle radical of 5 members or six membered-rings is desirable. As an example of a substituent, an aliphatic series radical, a halogen atom, an alkyl sulfonyl group, an aryl sulfonyl group, an acyl group, the acylamino radical, a sulfamoyl group, a carbamoyl group, an ionicity hydrophilic radical, etc. are contained. As an example of a heterocycle radical, 2-pyridyl radical, 2-thienyl group, 2-thiazolyl radical, 2-benzothiazolyl radical, 2-benzoxazolyl radical, and 2-furyl radical are contained.

[0161] As an example of said alkyl sulfonyl group and an aryl sulfonyl group, a methane sulfonyl group and a phenyl sulfonyl group can be mentioned respectively. As an example of said alkyl sulfinyl group and an aryl sulfinyl group, a methane sulfinyl group and a phenyl sulfinyl group can be mentioned respectively.

[0162] The acyl group which has a substituent, and a non-permuted acyl group are contained in said acyl group. As an acyl group, the acyl group of 1-12 has a desirable carbon atomic number. An ionicity hydrophilic radical is contained as an example of a substituent. An acetyl group and benzoyl are contained as an example of an acyl group.

[0163] An alkyl group, an aryl group, and the amino group permuted by the heterocycle radical are contained in said amino group, and, as for the alkyl group, the aryl group, and the heterocycle radical, you may have the substituent further. The non-permuted amino group is not contained. As an alkylamino radical, the alkylamino radical of the carbon atomic numbers 1-6 is desirable. An ionicity hydrophilic radical is contained as an example of a substituent. A methylamino radical and a diethylamino radical are mentioned as an example of an alkylamino radical. The arylamino radical which has a substituent, and a non-permuted arylamino radical are contained in said arylamino radical. As an arylamino radical, the arylamino radical of 6-12 has a desirable carbon atomic number. As an example of a substituent, a halogen atom and an ionicity hydrophilic radical are contained. As an example of an arylamino radical, an ANIRINO radical and 2-chloroanilino radical are contained.

[0164] The alkoxy group which has a substituent, and a non-permuted alkoxy group are contained in said alkoxy group. As an alkoxy group, the alkoxy group of 1-12 has a desirable carbon atomic number. As an example of a substituent, an alkoxy group, hydroxyl, and an ionicity hydrophilic radical are contained. As an example of an alkoxy group, a methoxy group, an ethoxy radical, an isopropoxy group, a methoxyethoxy radical, a hydroxy ethoxy radical, and 3-carboxy propoxy group are contained.

[0165] The aryloxy group which has a substituent, and a non-permuted aryloxy group are contained in said aryloxy

group. As an aryloxy group, the aryloxy group of 6-12 has a desirable carbon atomic number. As an example of a substituent, an alkoxy group and an ionicity hydrophilic radical are contained. As an example of an aryloxy group, a phenoxy group, p-methoxy phenoxy group, and o-methoxy phenoxy group are contained.

[0166] The acylamino radical which has a substituent is contained in said acylamino radical. As said acylamino radical, the acylamino radical of 2-12 has a desirable carbon atomic number. An ionicity hydrophilic radical is contained as an example of a substituent. As an example of the acylamino radical, an acetylamino radical, propionylamino radical, benzoylamino radical, N-phenylacetethylamino and 3, and 5-disulfo benzoylamino radical is contained.

[0167] The ureido radical which has a substituent, and a non-permuted ureido radical are contained in said ureido radical. As said ureido radical, the ureido radical of 1-12 has a desirable carbon atomic number. An alkyl group and an aryl group are contained as an example of a substituent. As an example of an ureido radical, 3-methyl ureido radical, 3, and 3-dimethyl ureido radical and 3-phenyl ureido radical are contained.

[0168] The sulfamoylamino group which has a substituent, and a non-permuted sulfamoylamino group are contained in said sulfamoylamino group. An alkyl group is contained as an example of a substituent. N and an N-dipropylsulfamoylamino radical are contained as an example of a sulfamoylamino group.

[0169] The alkoxycarbonylamino radical which has a substituent, and a non-permuted alkoxycarbonylamino radical are contained in said alkoxycarbonylamino radical. As an alkoxycarbonylamino radical, the alkoxycarbonylamino radical of 2-12 has a desirable carbon atomic number. An ionicity hydrophilic radical is contained as an example of a substituent. An ethoxycarbonylamino radical is contained as an example of an alkoxycarbonylamino radical.

[0170] The alkyl and the aryl sulfonylamino radical which are not permuted [the alkyl which has a substituent and an aryl sulfonylamino radical, and] are contained in said alkyl sulfonylamino radical and an aryl sulfonylamino radical. As alkyl and an aryl sulfonylamino radical, the alkyl and the aryl sulfonylamino radical of 1-12 have a desirable carbon atomic number. An ionicity hydrophilic radical is contained as an example of a substituent. As an example of alkyl and an aryl sulfonylamino radical, a methanesulfonylamino radical, N-phenylmethane sulfonylamino radical, a benzenesulphonyl amino radical, and 3-carboxy benzenesulphonyl amino radical are contained.

[0171] The carbamoyl group which has a substituent, and a non-permuted carbamoyl group are contained in said carbamoyl group. An alkyl group is contained as an example of a substituent. As an example of a carbamoyl group, a methyl carbamoyl group and a dimethyl carbamoyl group are contained.

[0172] The sulfamoyl group which has a substituent, and a non-permuted sulfamoyl group are contained in said sulfamoyl group. An alkyl group is contained as an example of a substituent. As an example of a sulfamoyl group, a dimethyl sulfamoyl group and a G (2-hydroxyethyl) sulfamoyl group are contained.

[0173] The alkoxy carbonyl group which has a substituent, and a non-permuted alkoxy carbonyl group are contained in said alkoxy carbonyl group. As an alkoxy carbonyl group, the alkoxy carbonyl group of 2-12 has a desirable carbon atomic number. An ionicity hydrophilic radical is contained as an example of a substituent. A methoxycarbonyl group and an ethoxycarbonyl radical are contained as an example of an alkoxy carbonyl group.

[0174] The acyloxy radical which has a substituent, and a non-permuted acyloxy radical are contained in said acyloxy radical. As an acyloxy radical, the acyloxy radical of the carbon atomic numbers 1-12 is desirable. An ionicity hydrophilic radical is contained as an example of a substituent. An acetoxy radical and a benzoyloxy radical are contained as an example of an acyloxy radical.

[0175] The carbamoyloxy radical which has a substituent, and a non-permuted carbamoyloxy radical are contained in said carbamoyloxy radical. An alkyl group is contained as an example of a substituent. An N-methylcarbamoyloxy radical is contained as an example of a carbamoyloxy radical.

[0176] The aryloxy carbonyl group which has a substituent, and a non-permuted aryloxy carbonyl group are contained in said aryloxy carbonyl group. As an aryloxy carbonyl group, the aryloxy carbonyl group of 7-12 has a desirable carbon atomic number. An ionicity hydrophilic radical is contained in a substituent. A phenoxy carbonyl group is contained as an example of an aryloxy carbonyl group.

[0177] The aryloxycarbonylamino radical which has a substituent, and a non-permuted aryloxycarbonylamino radical are contained in said aryloxycarbonylamino radical. As an aryloxycarbonylamino radical, the aryloxycarbonylamino radical of 7-12 has a desirable carbon atomic number. An ionicity hydrophilic radical is contained as an example of a substituent. A phenoxycarbonylamino radical is contained as an example of said aryloxycarbonylamino radical.

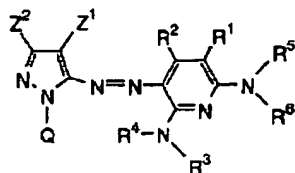
[0178] The alkyl, the aryl and the heterocycle thio radical which have a substituent, and non-permuted alkyl, aryl and a heterocycle thio radical are contained in said alkyl, aryl, and a heterocycle thio radical. As alkyl, aryl, and a heterocycle thio radical, the thing of 1-12 has a desirable carbon atomic number. An ionicity hydrophilic radical is contained as an example of a substituent. As an example of alkyl, aryl, and a heterocycle thio radical, a methylthio radical, a phenylthio radical, and a 2-pyridylthio group are contained.

[0179] In this invention, especially desirable azo dye is a compound expressed with the following general formula (M-II).

[0180]

[Formula 60]

一般式 (M-I)



[0181] In said general formula (M-II), as for Z1, Hammett's substituent constant σ value expresses 0.20 or more electron withdrawing groups. As for Z1, it is desirable that σ value is the electron withdrawing group of 0.30-1.0. Although the electron-attractive substituent later mentioned about a desirable concrete substituent can be mentioned, the acyl group of carbon numbers 2-12, the alkyloxy carbonyl group of carbon numbers 2-12, a nitro group, a cyano group, the alkyl sulfonyl group of carbon numbers 1-12, the aryl sulfonyl group of carbon numbers 6-18, the carbamoyl group of carbon numbers 1-12, and the alkyl halide radical of carbon numbers 1-12 are desirable especially. Especially desirable things are a cyano group, the alkyl sulfonyl group of carbon numbers 1-12, and the aryl sulfonyl group of carbon numbers 6-18, and the most desirable thing is a cyano group.

[0182] R1, R2, R5, and R6 are synonymous with the case of said general formula (M-I). R3 and R4 express a hydrogen atom, an aliphatic series radical, an aromatic series radical, a heterocycle radical, an acyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a carbamoyl group, an alkyl sulfonyl group, an aryl sulfonyl group, or a sulfamoyl group independently respectively. Also in it, a hydrogen atom, an aromatic series radical, a heterocycle radical, an acyl group, an alkyl sulfonyl group, and an aryl sulfonyl group are desirable, and a hydrogen atom, an aromatic series radical, and a heterocycle radical are especially desirable. Z2 expresses a hydrogen atom, an aliphatic series radical, an aromatic series radical, or a heterocycle radical. Q expresses a hydrogen atom, an aliphatic series radical, an aromatic series radical, or a heterocycle radical. Also in it, the radical of Q which consists of a nonmetal atom group required to form five to 8 membered-ring is desirable. This five to 8 membered-ring may be permuted, and even if it is a saturation ring, it may have the unsaturated bond. Also in it, an aromatic series radical and a heterocycle radical are desirable especially. As a desirable nonmetal atom, a nitrogen atom, an oxygen atom, a sulfur atom, and a carbon atom are mentioned. As an example of five to 8 membered-ring, the benzene ring, a cyclopentane ring, a cyclohexane ring, a cycloheptane ring, a cyclooctane ring, a cyclohexene ring, a pyridine ring, a pyrimidine ring, a pyrazine ring, a pyridazine ring, a triazine ring, an imidazole ring, a benzimidazole ring, an oxazole ring, a benzoxazole ring, a thiazole ring, a benzothiazole ring, an oxane ring, a sulfolane ring, the Jiang ring, etc. mention, and it is ****, for example.

[0183] Each radical explained by said general formula (M-II) may have the substituent further. When each of these radicals have a substituent further, as this substituent, the substituent explained by said general formula (M-I), the radical illustrated by G, R1, and R2, and an ionicity hydrophilic radical are mentioned.

[0184] here, in relation to a substituent Z1, Hammett's substituent constant σ value used by this detail letter is explained. Although a Hammett rule is a rule of thumb advocated by L.P.Hammett in 1935 in order to discuss quantitatively the effect of the substituent exerted on the reaction or balance of a benzene derivative, as for this, validity is accepted widely today. Although there are σ value and σ_m value in the substituent constant for which the Hammett rule was asked and these values can be found out to many common compendiums, it will be detailed in the volume on J.A.Dean, the 12th edition, 1979 (McGraw-Hill) and a "Lange's Handbook of Chemistry" "chemical field" special number, No. 122, 96-103 pages, and 1979 (Nankodo), for example. In addition, although each substituent is limited by Hammett's substituent constant σ or is explained in this invention, even if not the semantics that this is limited only to a substituent with the value of reference known which can be found out with the above-mentioned compendium but the value is reference strangeness, when it measures based on a Hammett rule, it cannot be overemphasized that the substituent which will be wrapped within the limits of it is also included. moreover, the general formula (M-I) of this invention -- and (M-II) uses σ value regardless of a permutation location as a scale which shows the electronic effectiveness of a substituent, although the object which is not a benzene derivative is also contained in inside. In this invention, σ value is used in such semantics.

[0185] a Hammett substituent constant σ value -- as 0.60 or more electron withdrawing groups -- a cyano group, a nitro group, and an alkyl sulfonyl group -- [-- for example, a methane sulfonyl group and an aryl sulfonyl group (for example, benzenesulphonyl radical) can be mentioned as an example.) A Hammett σ value as 0.45 or more electron withdrawing groups It adds above. An acyl group (for example, acetyl group), an alkoxy carbonyl group (For example, a dodecyloxy carbonyl group), an aryloxy carbonyl group (For example, m-chloro phenoxy carbonyl group), an alkyl sulfinyl group (For example, n-propyl sulfinyl group), an aryl sulfinyl group (For example, a phenyl sulfinyl

group), a sulfamoyl group (for example, N-ethyl sulfamoyl group, N, and N-dimethyl sulfamoyl group), and an alkyl halide radical (for example, TORIFURORO methyl group) can be mentioned.

[0186] A Hammett substituent constant σ value as 0.30 or more electron withdrawing groups It adds above. An acyloxy radical (for example, acetoxy radical), a carbamoyl group (For example, N-ethyl carbamoyl group, N, and N-dibutyl carbamoyl group), A halogenation alkoxy group (for example, truffe ROROME chill oxy-radical), a halogenation aryloxy group (For example, a pen TAFURORO phenyloxy radical), a sulfonyloxy radical (For example, a methyl sulfonyloxy radical), a halogenation alkylthio group (For example, a JIFURORO methylthio radical), the aryl group by which two or more σ values were permuted by 0.15 or more electron withdrawing groups For example, (a 2,4-dinitrophenyl radical and a pentachlorophenyl group), and heterocycle (for example, 2-benzoxazolyl radical, 2-benzothiazolyl radical, a 1-phenyl 2-benzimidazolyl radical) can be mentioned. In addition to the above, σ value is mentioned for a halogen atom etc. as an example of 0.20 or more electron withdrawing groups.

[0187] The combination of a substituent especially desirable as a compound expressed with said general formula (M-I) is as follows.

(b) It is a hydrogen atom, an alkyl group, an aryl group, a heterocycle radical, a sulfonyl group, and an acyl group preferably, and R5 and R6 are a hydrogen atom, an aryl group, a heterocycle radical, and a sulfonyl group still more preferably, and they are a hydrogen atom, an aryl group, and a heterocycle radical most preferably. However, neither R5 nor R6 are a hydrogen atom.

(b) G is a hydrogen atom, a halogen atom, an alkyl group, hydroxyl, an amino group, and an amide group preferably, is a hydrogen atom, a halogen atom, an amino group, and an amide group still more preferably, and is a hydrogen atom, an amino group, and an amide group most preferably.

(c) A is a pyrazole ring, an imidazole ring, an iso thiazole ring, a thiadiazole ring, and a benzothiazole ring preferably, is a pyrazole ring and an iso thiazole ring still more preferably, and is a pyrazole ring most preferably.

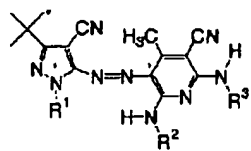
(d) B1 and B-2 are =CR1- and -CR2= respectively, and respectively, these [R1 and R2] are a hydrogen atom, a halogen atom, a cyano group, a carbamoyl group, a carboxyl group, an alkyl group, hydroxyl, and an alkoxy group preferably, and are a hydrogen atom, a cyano group, a carbamoyl group, and an alkoxy group still more preferably.

[0188] In addition, about the combination of the desirable substituent of a compound expressed with a general formula (M-I), the compound whose at least one of the various substituents is the aforementioned desirable radical is desirable, the compound many whose various substituents are said desirable radicals more is more desirable, and the compound all whose substituents are said desirable radicals is the most desirable.

[0189] Although the instantiation compound (a-1 to a-27, b-1 to b-6, c-1 to c-3, d-1 to d-4, e-1 to e-4) of the compound expressed with said general formula (M-I) is shown below, this invention is not limited to the following example.

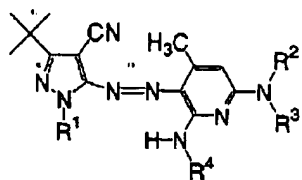
[0190]

[Formula 61]



染料	R ¹	R ²	R ³
a-1			
a-2			
a-3			
a-4			
a-5			
a-6			
a-7			
a-8			
a-9			
a-10			

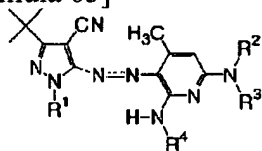
[0191]
[Formula 62]



染料	R ¹	R ²	R ³	R ⁴
a-11				
a-12		SO ₂ CH ₃		
a-13		COCH ₃	C ₈ H ₁₇ (l)	C ₈ H ₁₇ (l)
a-14				
a-15		SO ₂ CH ₃		C ₈ H ₁₇ (l)

[0192]

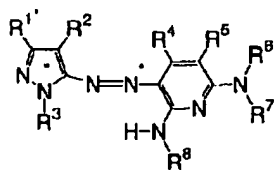
[Formula 63]



染料	R ¹	R ²	R ³	R ⁴
a-16				
a-17				
a-18				
a-19			OC ₁₂ H ₂₅	OC ₁₂ H ₂₅
a-20				C ₈ H ₁₇ (l)

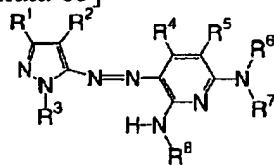
[0193]

[Formula 64]



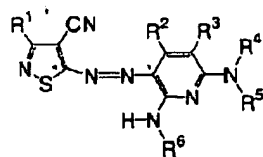
染料	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	R ⁷	R ⁸
a-21		CN		H	CONH ₂	SO ₂ CH ₃		
a-22		Br		COOC ₂ H ₅	H		C ₈ H ₁₇ (l)	COCH ₃
a-23		SO ₂ CH ₃		CONH ₂	H			CO-
a-24		CN		H	H			SO ₂ CH ₃

[0194]
[Formula 65]



染料	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	R ⁷	R ⁸
a-25		Br		H	CONH ₂	COCH ₃		
a-26		CN		CH ₃	H			
a-27		CN		CH ₃	CN	H		

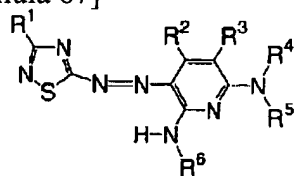
[0195]
[Formula 66]



染料	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶
b-1	CH ₃	CH ₃	CN	H		
b-2	CH ₃	CH ₃	CN	H		
b-3	CH ₃	CH ₃	CONH ₂	H		
b-4	CH ₃	CH ₃	H	H		
b-5	CH ₃	CH ₃	H			
b-6	CH ₃	CH ₃	H			

[0196]

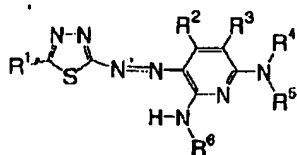
[Formula 67]



染料	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶
c-1	SCH ₃	CH ₃	CN	H	C ₈ H ₁₇ (l)	
c-2	CH ₃	CH ₃	H			
c-3		H	H			C ₈ H ₁₇ (l)

[0197]

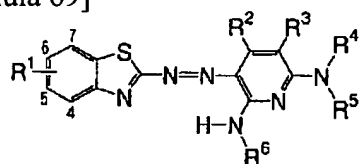
[Formula 68]



染料	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶
d-1	CH ₃	CH ₃	CN	H		
d-2	CH ₃	H	H			
d-3		CH ₃	CONH ₂	H		
d-4		CH ₃	H			

[0198]

[Formula 69]

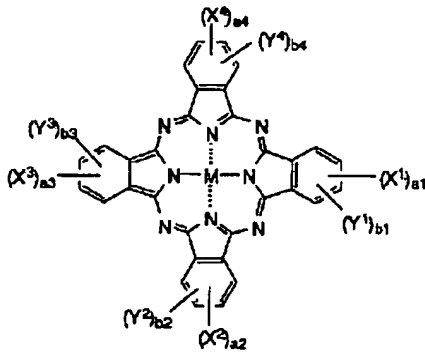


染料	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶
e-1	5-Cl	CH ₃	CONH ₂	H	C ₈ H ₁₇ (t)	C ₈ H ₁₇ (t)
e-2	5,6-diCl	H	H			
e-3	5,6-diCl	CH ₃	H			COCH ₃
e-4	5-NO ₂	CH ₃	H	SO ₂ CH ₃		

[0199] It is desirable to use the compound (for "phthalocyanine dye" to be called hereafter) expressed with the following general formula (C-I) as oil solubility coloring matter in this invention. The compound expressed with a general formula (C-I) below is explained.

[0200]

[Formula 70]



[0201] In said general formula (C-I), X1, X2, X3, and X4 express -SO-Z1, -SO2-Z1, or -SO2NR²¹R²² independently respectively.

[0202] The heterocycle radical which is not permuted [aryl group / which is not permuted / aralkyl radical / which be permuted / alkenyl radical / which be permuted / cycloalkyl radical / which be permuted / alkyl group / permuted / permutation or / , permutation, or / , permutation, or / , permutation, or / , permutation, or / , permutation, or] expresses, it is especially desirable in the heterocycle radical which is not permuted [aryl group / which be permuted / alkyl group / which be permuted / permutation or / , permutation, or / , permutation, or, and it the most desirable in a terrorism ring machine to a permutation alkyl group, a permutation aryl group, and a permutation also in it. / 1 / Z

[0203] Respectively R21 and R22 independently The alkyl group which is not permuted [a hydrogen atom, a permutation, or], The alkenyl radical which is not permuted [the cycloalkyl radical which is not permuted / a permutation or /, a permutation, or], The aryl group which is not permuted [the aralkyl radical which is not permuted / a permutation or / a permutation, or], The heterocycle radical which is not permuted [a permutation or] is expressed, the heterocycle radical which is not permuted [the aryl group which is not permuted / the alkyl group which is not permuted / a hydrogen atom, a permutation, or /, a permutation, or /, a permutation, or] is especially desirable, and a terrorism ring machine is the most desirable to a hydrogen atom, a permutation alkyl group, a permutation aryl group, and a permutation also in it. However, both R21 and R22 are hydrogen atoms.

[0204] The alkyl group of 1-30 has [the alkyl group of a permutation or no permuting which R21, R22, and Z1 express] a desirable carbon atomic number. The same thing as a substituent when the below-mentioned Z1, R21, R22, Y1, Y2, Y3, and Y4 are able to have a substituent further as an example of a substituent is mentioned. Also in these, hydroxyl, an alkoxy group, a cyano group, and a halogen atom are desirable.

[0205] The cycloalkyl radical of 5-30 has [the cycloalkyl radical which R21, R22, and Z1 express and which has a substituent, or a non-permuted cycloalkyl radical] a desirable carbon atomic number. The same thing as a substituent when the below-mentioned Z1, R21, R22, Y1, Y2, Y3, and Y4 are able to have a substituent further as an example of a substituent is mentioned. Especially, hydroxyl, an alkoxy group, a cyano group, and a halogen atom are desirable.

[0206] The alkenyl radical of 2-30 has [the alkenyl radical which R21, R22, and Z1 express and which has a substituent, or a non-permuted alkenyl radical] a desirable carbon atomic number. The same thing as a substituent when the below-mentioned Z1, R21, R22, Y1, Y2, Y3, and Y4 are able to have a substituent further as an example of a substituent is mentioned. Especially, hydroxyl, an alkoxy group, a cyano group, and a halogen atom are desirable.

[0207] The aralkyl radical of 7-30 has [the aralkyl radical which R21, R22, and Z1 express and which has a substituent, or a non-permuted aralkyl radical] a desirable carbon atomic number. The same thing as a substituent when the below-mentioned Z1, R21, R22, Y1, Y2, Y3, and Y4 are able to have a substituent further as an example of a substituent is mentioned. Especially, hydroxyl, an alkoxy group, a cyano group, and a halogen atom are desirable.

[0208] the same as a substituent when the below-mentioned Z1, R21, R22, Y1, Y2, Y3, and Y4 are able to have a substituent further as a substituent of the aryl group which R21, R22, and Z1 express -- it is mentioned. As a desirable substituent, a halogen atom, a heterocycle radical, a cyano group, hydroxyl, A nitro group, a carboxyl group, the acylamino radical, an ureido radical, a sulfamoylamino group, An alkyloxy carbonyl group, an alkyloxy carbonylamino radical, A sulfonamide radical, a sulfamoyl group, a carbamoyl group, a sulfonyl group, An acyloxy radical, a carbamoyloxy radical, an imide radical, a heterocycle thio radical, An acyl group, a sulfonic group, and the 4th class ammonium are mentioned. Especially A heterocycle radical, A cyano group, a carboxyl group, the acylamino radical, a sulfonamide radical, a sulfamoyl group, A carbamoyl group, a sulfonyl group, an imide radical, and an acyl group are desirable, and a cyano group, a carboxyl group, a sulfamoyl group, a carbamoyl group, a sulfonyl group, an imide radical, and an acyl group are still more desirable.

[0209] As a heterocycle radical which R21, R22, and Z1 express, the thing of 5 members or six membered-rings is

desirable, and they may be condensing the ring further. Moreover, it may be aromatic series heterocycle or you may be non-aromatic heterocycle. Although a permutation location is omitted and the heterocycle radical expressed with R21, R22, and Z1 below is illustrated in the form of heterocycle, a permutation location is not limited, and if it is a pyridine, it can be permuted by the 2nd place, the 3rd place, and the 4th place. A pyridine, pyrazine, a pyrimidine, pyridazine, triazine, a quinoline, An isoquinoline, quinazoline, cinnoline, phthalazine, quinoxaline, A pyrrole, Indore, a furan, benzofuran, a thiophene, benzothiophene, A pyrazole, an imidazole, benzimidazole triazole, oxazole, Benzoxazole, a thiazole, benzothiazole, an iso thiazole, a bends iso thiazole, thiadiazole, an isoxazole, benzisoxazole, a pyrrolidine, a piperidine, a piperazine, imidazolidine, thiazoline, etc. are mentioned. If an aromatic series heterocycle radical is desirable and illustrates that desirable example as the point similarly in this, a pyridine, pyrazine, a pyrimidine, pyridazine, triazine, a pyrazole, an imidazole, benzimidazole triazole, a thiazole, benzothiazole, an iso thiazole, a bends iso thiazole, and thiadiazole will be mentioned. These may have the substituent.

[0210] Respectively Y1, Y2, Y3, and Y4 independently A hydrogen atom, a halogen atom, An alkyl group, a cycloalkyl radical, an alkenyl radical, an aralkyl radical, an aryl group, A heterocycle radical, a cyano group, hydroxyl, a nitro group, the amino group, an alkylamino radical, An alkoxy group, an aryloxy group, an amide group, an arylamino radical, an ureido radical, A sulfamoylamino group, an alkylthio group, an aryl thio radical, an alkoxy-carbonylamino radical, A sulfonamide radical, a carbamoyl group, a sulfamoyl group, a sulfonyl group, An alkoxy carbonyl group, a heterocycle oxy-radical, azo, an acyloxy radical, A carbamoyloxy radical, a silyloxy radical, an aryloxy carbonyl group, an aryloxy-carbonylamine radical, an imide radical, a heterocycle thio radical, a phosphoryl group, an acyl group, a carboxyl group, or a sulfonic group may be expressed, and each may have the substituent further.

[0211] Also in these, a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a cyano group, an alkoxy group, an amide group, an ureido radical, a sulfonamide radical, a carbamoyl group, a sulfamoyl group, and an alkoxy carbonyl group are desirable, a hydrogen atom, a halogen atom, and a cyano group are especially desirable, and a hydrogen atom is the most desirable.

[0212] When it is a radical with Z1, R21, R22, Y1, Y2, Y3, and Y4 [able to have a substituent further], you may have further a substituent which was listed to below.

[0213] The straight chain or branched chain alkyl group of a halogen atom (for example, a chlorine atom, a bromine atom) and carbon numbers 1-30, The straight chain or branched chain alkynyl group of the aralkyl radical of carbon numbers 7-30, the alkenyl radical of carbon numbers 2-30, and carbon numbers 2-30, By the straight chain of the straight chain of carbon numbers 3-30 or a branched chain cycloalkyl radical, and carbon numbers 3-30, or the branched chain cyclo alkenyl radical detailed (for example, methyl, ethyl, propyl, isopropyl, and t-butyl --) 2-methane sulfonyl ethyl, 3-phenoxy propyl, trifluoromethyl, cyclopentyl and an aryl group (for example, phenyl and 4-t-butylphenyl --) 2, 4-G t-amyl phenyl, and a heterocycle radical (for example, imidazolyl --) Pyrazolyl, thoria ZORIRU, 2-furil, 2-thienyl, 2-pyrimidinyl, 2-benzothiazolyl, a cyano group, hydroxyl, a nitro group, a carboxy group, the amino group and an alkyloxy radical (for example, methoxy and ethoxy **2-methoxyethoxy --) 2-methane sulfonyl ethoxy and an aryloxy group (for example, phenoxy --) 2-methylphenoxy, 4-t-butyl phenoxy, 3-nitro phenoxy, 3-t-butyloxy carbamoyl phenoxy, 3-methoxy carbamoyl, The acylamino radical (for example, an acetamide, a benzamide, 4-(3-t-butyl-4-hydroxy phenoxy) butaneamide), an alkylamino radical (for example, methylamino, butylamino, and diethylamino --) methylbutylamino and an ANIRINO radical (for example, phenylamino and 2-chloroanilino --) An ureido radical (for example, phenyl ureido, methyl ureido, N, and N-dibutyl ureido), A sulfamoylamino group (for example, N, N-dipropylsulfamoylamino), An alkylthio group (for example, a methylthio, octylthio, 2-phenoxy ethyl thio), an aryl thio radical (for example, phenylthio and 2-butoxy-5-t-octyl phenylthio --) 2-carboxy phenylthio, an alkyloxy carbonylamino radical (For example, methoxycarbonylamino), a sulfonamide radical For example, (a methanesulfonamide, benzenesulfonamide, p-toluenesulfonamide), A carbamoyl group (for example, N-ethyl carbamoyl, N, and N-dibutyl carbamoyl), a sulfamoyl group (for example, N-ethyl sulfamoyl, N, and N-dipropyl sulfamoyl --) N-phenyl sulfamoyl and a sulfonyl group (for example, a methane sulfonyl --) An octane sulfonyl, benzenesulphonyl, tosyl, An alkyloxy carbonyl group (for example, methoxycarbonyl, butyloxy carbonyl), Heterocycle oxy-radical (for example) [1-phenyl tetrazole-5-oxy-**] 2-tetrahydropyranloxy and azo (for example, phenylazo --) 4-methoxy phenylazo, 4-pivaloyl amino phenylazo, 2-hydroxy-4-propanoyl phenylazo, An acyloxy radical (for example, acetoxy), a carbamoyloxy radical For example, (N-methylcarbamoyloxy, N-phenylcarbamoyloxy), A silyloxy radical (for example, trimethylsilyloxy, dibutyl methyl silyloxy), An aryloxy-carbonylamine radical (for example, phenoxy-carbonylamino), An imide radical (for example, N-succinimide, N-phthalimide), a heterocycle thio radical for example, 2-benzothiazolethio, 2, and 4-G phenoxy - 1, 3, and 5-triazole-6-thio -- 2-pyridylthio, a sulfinyl group (for example, 3-phenoxy propyl sulfinyl), a phosphonyl group (for example, phenoxy phosphonyl and octyloxy phosphonyl --) Phenyl phosphonyl, an aryloxy carbonyl group (for example, phenoxy carbonyl), An acyl group (for example, acetyl, 3-phenyl propanoyl, benzoyl), an ionicity hydrophilic radical (for example, a carboxyl group, a sulfonic group,

and the 4th class ammonium), etc. are mentioned.

[0214] a1-a4, and b1-b4 express the number of substituents of X1-X4, and Y1-Y4 respectively, a1-a4 express the integer of 0-4 independently respectively, and b1-b4 express the integer of 0-4 independently respectively. However, total of a1-a4 is two or more. Here, when a1-a4, and b1-b4 express two or more integers, even if two or more X1-X4, and Y1-Y4 are respectively the same, they may differ.

[0215] each with which a1 and b1 fill the relation of $a1+b1=4$ -- the independent integer of 0-4 is expressed, it combines and comes out and especially a desirable thing has the most desirable combination as which a1 expresses 1 or 2, and b1 expresses 3 or 2 and as which it is, a1 expresses 1 also in it, and b1 expresses 3.

[0216] each with which a2 and b2 fill the relation of $a2+b2=4$ -- the independent integer of 0-4 is expressed, it combines and comes out and especially a desirable thing has the most desirable combination as which a2 expresses 1 or 2, and b2 expresses 3 or 2 and as which it is, a2 expresses 1 also in it, and b2 expresses 3.

[0217] each with which a3 and b3 fill the relation of $a3+b3=4$ -- the independent integer of 0-4 is expressed, it combines and comes out and especially a desirable thing has the most desirable combination as which a3 expresses 1 or 2, and b3 expresses 3 or 2 and as which it is, a3 expresses 1 also in it, and b3 expresses 3.

[0218] each with which a4 and b4 fill the relation of $a4+b4=4$ -- the independent integer of 0-4 is expressed, it combines and comes out and especially a desirable thing has the most desirable combination as which a4 expresses 1 or 2, and b4 expresses 3 or 2 and as which it is, a4 expresses 1 also in it, and b4 expresses 3.

[0219] M expresses a hydrogen atom, a metallic element or its oxide, a hydroxide, or a halogenide. As a hydrogen atom and a metal atom, as for a thing desirable as M, Li, Na, K, Mg, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, nickel, Ru, Rh, Pd, Os, Ir, Pt, Cu, Ag, Au, Zn, Cd, Hg, aluminum, Ga, In, Si, germanium, Sn, Pb, Sb, Bi, etc. are mentioned. VO, GeO, etc. are mentioned as an oxide. Moreover, as a hydroxide, Si(OH)₂, Cr(OH)₂, and Sn(OH)₂ grade are mentioned. Furthermore, as a halogenide, AlCl, SiCl₂, VCl and VCl₂, VOCl, FeCl, GaCl, ZrCl, etc. are mentioned. Also especially in these, Cu, nickel, Zn, aluminum, etc. are desirable and Cu is the most desirable.

[0220] Moreover, Pc (phthalocyanine ring) may form a dimer (for example, Pc-M-L-M-Pc) or a trimer through L (divalent connection radical), and M in that case may be the same respectively, or may differ.

[0221] The divalent connection radical expressed with L has an oxy-radical (-O-), a thio radical (-S-), a carbonyl group (-CO-), a sulfonyl group (-SO₂-), an imino group (-NH-), or a desirable methylene group (-CH₂-).

[0222] The combination especially desirable as a compound expressed with said general formula (C-I) is as follows.

[0223] Especially as X1-X4, -SO₂-Z1 or -SO₂NR₂₁R₂₂ is respectively desirable independently.

[0224] Independently, Z1 has the desirable heterocycle radical which is not permuted [the aryl group which is not permuted / the alkyl group which is not permuted / a permutation or /, a permutation, or /, a permutation, or], and its a terrorism ring machine is respectively the most desirable to a permutation alkyl group, a permutation aryl group, and a permutation also in it.

[0225] Independently, R₂₁ and R₂₂ have the desirable heterocycle radical which is not permuted [the aryl group which is not permuted / the alkyl group which is not permuted / a hydrogen atom a permutation, or /, a permutation, or /, a permutation, or], and its a terrorism ring machine is respectively the most desirable to a hydrogen atom, a permutation alkyl group, a permutation aryl group, and a permutation also in it.

[0226] Y1-Y4 have a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a cyano group, an alkoxy group, an amide group, an ureido radical, a sulfonamide radical, a carbamoyl group, a sulfamoyl group, an alkoxy carbonyl group, a carboxyl group, and a desirable sulfonic group, a hydrogen atom, a halogen atom, a cyano group, a carboxyl group, and its a sulfonic group are especially desirable, and its a hydrogen atom is the most desirable.

[0227] Independently, as for a1-a4, it is desirable that it is 1 or 2, and it is respectively desirable that it is especially 1. Independently, as for b1-b4, it is desirable that it is 3 or 2, and it is respectively desirable that it is especially 3.

[0228] M expresses a hydrogen atom, a metallic element or its oxide, a hydroxide, or a halogenide, Cu, nickel, Zn, and its aluminum are especially desirable, and its Cu is especially the most desirable also in especially inside.

[0229] About the combination of the desirable substituent of a compound expressed with said general formula (C-I), the compound whose at least one of the various substituents is the aforementioned desirable radical is desirable, the compound many whose various substituents are said desirable radicals more is more desirable, and the compound all whose substituents are said desirable radicals is the most desirable.

[0230] Also in the compound expressed with said general formula (C-I), the compound of the structure expressed with the following general formula (C-II) is more desirable.

[0231]

[Formula 71]

[0233] Specifically, X11, and X12, X13 and X14 express -SO-Z11, -SO₂-Z11, or -SO₂NR 23R24 independently respectively among said general formula (C-II). Z11 expresses the heterocycle radical which is not permuted [the aryl group which is not permuted / the aralkyl radical which is not permuted / the alkenyl radical which is not permuted / the cycloalkyl radical which is not permuted / the alkyl group which is not permuted / a permutation or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or]. R23 The cycloalkyl radical which is not permuted [the alkyl group which is not permuted / a hydrogen atom, a permutation, or /, a permutation, or], The heterocycle radical which is not permuted [the aryl group which is not permuted / the aralkyl radical which is not permuted / the alkenyl radical which is not permuted / a permutation or /, a permutation, or /, a permutation, or /, a permutation, or] is expressed. R24 The heterocycle radical which is not permuted [the aryl group which is not permuted / the aralkyl radical which is not permuted / the alkenyl radical which is not permuted / the cycloalkyl radical which is not permuted / the alkyl group which is not permuted / a permutation or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or] is expressed. Y11, Y12, Y13, Y14, Y15, Y16, Y17, and Y18 Independently respectively A hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl radical, An alkenyl radical, an aralkyl radical, an aryl group, a heterocycle radical, a cyano group, Hydroxyl, a nitro group, the amino group, an alkylamino radical, an alkoxy group, An aryloxy group, an amide group, an arylamino radical, an ureido radical, a sulfamoylamino group, An alkylthio group, an aryl thio radical, an alkoxycarbonylamino radical, A sulfonamide radical, a carbamoyl group, an alkoxy carbonyl group, a heterocycle oxy-radical, Azo, an acyloxy radical, a carbamoyloxy radical, a silyloxy radical, An aryloxy carbonyl group, an aryloxycarbonylamine radical, an imide radical, a heterocycle thio radical, a phosphoryl group, an acyl group, a carboxyl group, or a sulfonic group may be expressed, and each radical may have the substituent further. Although a11-a14 express the number of substituents of X11-X14 respectively and the integer of 0-2 is expressed independently respectively, all are not set to 0 to coincidence. In addition, when a11-a14 express 2, even if two X11-X14 are respectively the same, they may differ. M1 is a hydrogen atom, a metallic element or its oxide, a hydroxide, or a halogenide.

[0239] Independently, R24 has the desirable heterocycle radical which is not permuted [the aryl group which is not permuted / the alkyl group which is not permuted / a permutation or /, a permutation, or /, a permutation, or], and its a terrorism ring machine is respectively the most desirable to a permutation alkyl group, a permutation aryl group, and a

permutation also in it.

[0240] Independently, Y11-Y18 have a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a cyano group, an alkoxy group, an amide group, an ureido radical, a sulfonamide radical, a carbamoyl group, a sulfamoyl group, and a desirable alkoxy carbonyl group, a hydrogen atom, a halogen atom, and its a cyano group are especially desirable, and its a hydrogen atom is respectively the most desirable.

[0241] As for a11-a14, it is respectively desirable independently that it is 1 or 2, and it is desirable that especially all are 1.

[0242] M1 expresses a hydrogen atom, a metallic element or its oxide, a hydroxide, or a halogenide, Cu, nickel, Zn, and its aluminum are especially desirable, and its Cu is the most desirable also in it.

[0243] About the combination of the desirable substituent of a compound expressed with said general formula (C-II), the compound whose at least one of the various substituents is the aforementioned desirable radical is desirable, the compound many whose various substituents are said desirable radicals more is more desirable, and the compound all whose substituents are said desirable radicals is the most desirable.

[0244] With the synthesis method, the compound expressed with said general formula (C-I) has the common case where it is the analog mixture with which the introductory location and the introductory number of Substituents R_n (n=1-4) and Y_q (q=1-4) differ from each other unescapable, equalizes these analog mixture statistically and expresses it in many cases. This invention will find out that especially specific mixture is desirable, if such analog mixture is classified into three kinds shown below.

[0245] In this invention, the phthalocyanine system coloring matter analog mixture which is said general formula (C-I) and (C-II) a compound expressed is classified and defined as the following three kinds based on a permutation location.

[0246] (1) At least beta- is a permutation mold. : (phthalocyanine dye which has 2 and/or the 3rd place, 6 and/or the 7th place, 10 and/or the 11th place, 14, and/or a specific substituent in the 15th place)

[0247] (2) At least alpha- is a permutation mold. : (phthalocyanine dye which has 1 and/or the 4th place, 5 and/or the 8th place, 9 and/or the 12th place, 13, and/or a specific substituent in the 16th place)

[0248] (3) At least alpha and beta- are a mixed permutation mold. : (phthalocyanine dye which has a specific substituent irregular in the 1-16th place)

[0249] When explaining the derivative of phthalocyanine dye with which structures differ in this specification (especially permutation location), at least above-mentioned beta- uses [a permutation mold, alpha, and beta-] a mixed permutation mold at least for a permutation mold and alpha-.

[0250] The phthalocyanine derivative used for this invention is compoundable combining an approach similar to a publication, a citation, or these to Shiroy-Kobayashi collaboration, IPC Issue "phthalocyanine-chemistry and function -" (P. 1-62), C.C.Leznoff-A.B.P.Lever collaboration, and VCH issue 'Phthalocyanines-Properties and Applications' (P. 1-54) etc.

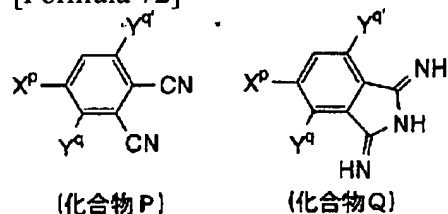
[0251] the compound expressed with the general formula (C-I) of this invention -- WO 00/17275 -- said -- 00/08103 -- said -- 00/08101 -- said -- pass sulfonation of a non-permuted phthalocyanine compound, the formation of sulfonyl chloride, and an amidation reaction so that it is indicated by each official report of 98/41853 and JP,10-36471,A etc. -- it is compoundable. In this case, the number which sulfonation may take place upwards in every location of a phthalocyanine nucleus, and is sulfonated is also difficult to control. Therefore, when a sulfonic group is introduced by such reaction condition, the location and the number of a sulfonic group which were introduced into the product cannot be specified, but give the mixture with which the number of a substituent surely differs from a permutation location. Therefore, since the number or the permutation location of a heterocycle permutation sulfamoyl group cannot be pinpointed when compounding the compound of this invention by making it into a raw material, at least alpha and beta- in which some kinds of compounds with which the number of a substituent differs from a permutation location as a compound of this invention are contained are obtained as mixed permutation mold mixture.

[0252] If many electron withdrawing groups like a sulfamoyl group are introduced into a phthalocyanine nucleus as mentioned above for example, oxidation potential will serve as ** more and ozone resistance will increase. If the above-mentioned synthesis method is followed, there will be little number into which the electron withdrawing group is introduced, namely, it will not be avoided that the phthalocyanine dye whose oxidation potential is ** more mixes. Therefore, in order to raise ozone resistance, it is more desirable to use a synthesis method which suppresses generation of the compound whose oxidation potential is ** more.

[0253] The compound expressed with the general formula (C-II) of this invention can be guided to it from the compound which the phthalonitrile derivative (compound P) and/or diimino iso indoline derivative (compound Q) which are expressed for example, with the following type are made to react with the metal derivative expressed with the following general formula (C-III), and is obtained.

[0254]

[Formula 72]



[0255] p expresses 11-14 among Compounds P and Q, and q and q' expresses 11-18 independently respectively.

[0256] General formula (C-III)

M-(Y) In the d aforementioned general formula (C-III), M is synonymous with M in said general formula (C-I) and (C-II) compound expressed, Y expresses a ligand univalent [, such as a halogen atom, an acetic-acid anion, acetylacetonate, and oxygen,] or divalent, and d expresses the integer of 1-4.

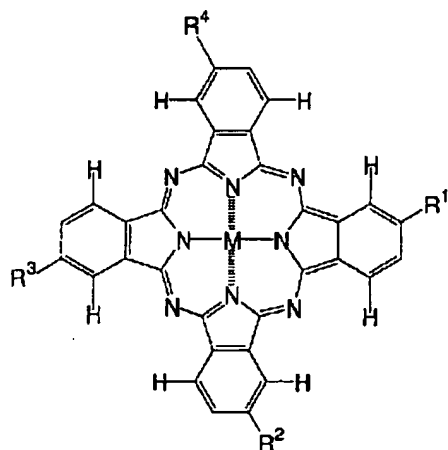
[0257] That is, if the above-mentioned synthesis method is followed, only a specific number can introduce the substituent of a wish. In order to make oxidation potential high like this invention especially, the above-mentioned synthesis method is extremely excellent as compared with the synthesis method of a compound expressed with a general formula (C-I) to introduce many electron withdrawing groups.

[0258] The mixture of the compound by which the compound expressed with said general formula (C-II) obtained in this way is expressed with following general formula (C-II -1) - (C-II -4) which is usually an isomer in each permutation location of Xp, i.e., beta-, serves as a permutation mold (2 and or the 3rd place, 6 and or the 7th place, 10 and or the 11th place, 14 and or phthalocyanine dye which has a specific substituent in the 15th place).

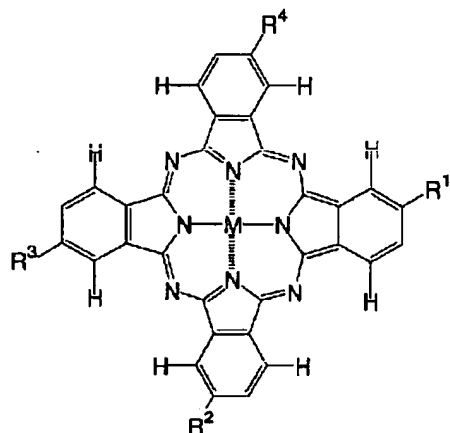
[0259]

[Formula 73]

一般式 (C-11-1)



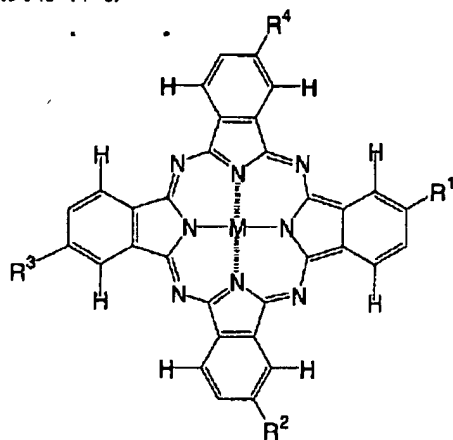
一般式 (C-11-2)



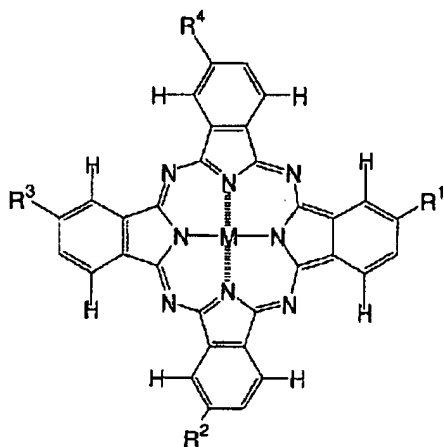
[0260]

[Formula 74]

一般式 (C-11-3)



一般式 (C-11-4)



[0261] In said general formula (C-II -1) - (C-II -4), R1-R4 are synonymous with a11-(X14) a14 in said general formula (C-II) (X11).

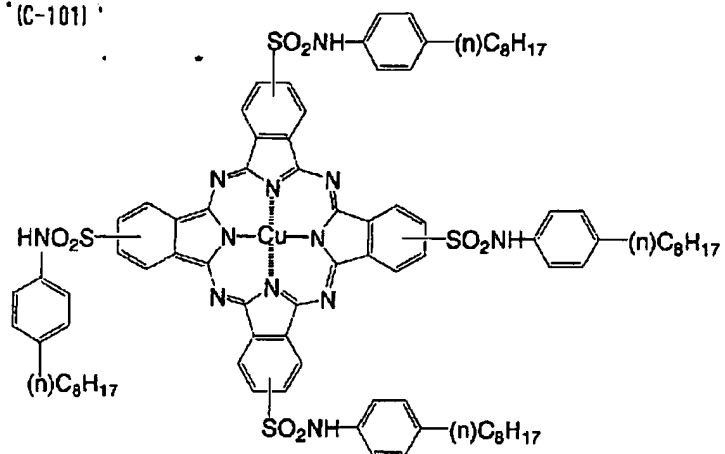
[0262] In this invention, it is found out also in which permutation mold that it is very important for improvement in robustness that oxidation potential is ** from 1.0V (vs S C E). At least alpha and beta- are in the inclination at least for beta- to excel the mixed permutation mold in a hue, light fastness, ozone gas resistance, etc. in the permutation mold, especially.

[0263] Although said general formula (C-I) or (C-II) the instantiation compound (C-101 to C-120) of a compound expressed is shown below, this invention is not limited to the following example.

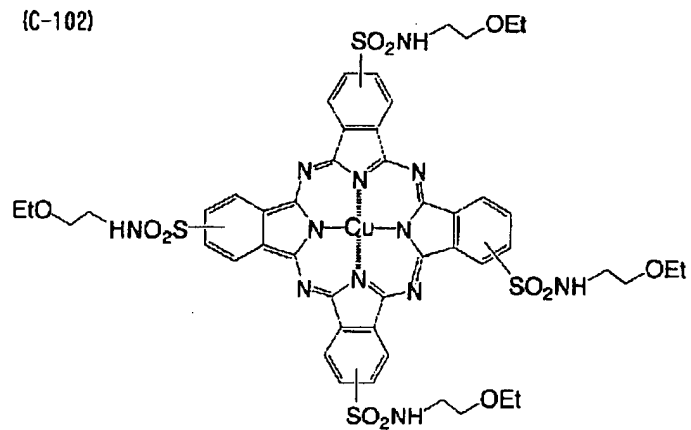
[0264]

[Formula 75]

{C-101}



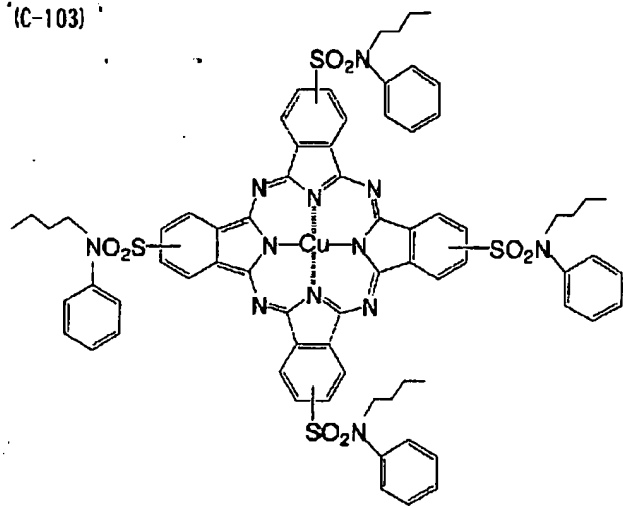
{C-102}



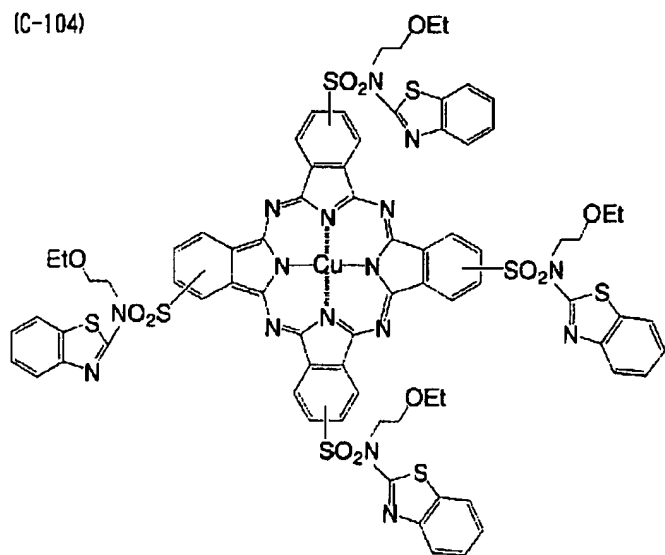
[0265]

[Formula 76]

(C-103)

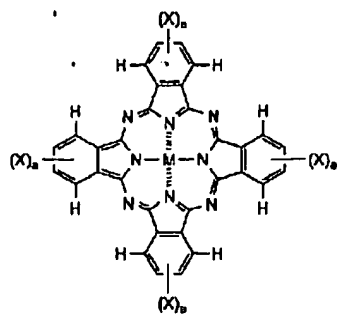


(C-104)



[0266]

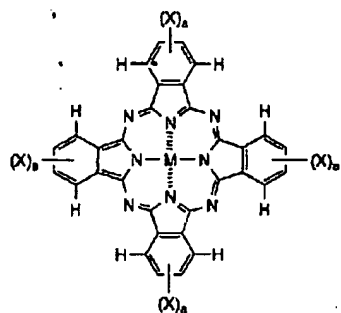
[Formula 77]



化合物 No.	M	X	a
C-105	Cu	$-\text{SO}_2\text{NHC}_8\text{H}_{17}(\text{t})$	1
C-106	Cu		1
C-107	Cu		1
C-108	Cu		1
C-109	Cu		1
C-110	Cu	$-\text{SO}_2\text{N}(\text{C}_6\text{H}_{11})_2$	1
C-111	Cu		1
C-112	Cu	$-\text{SO}_2\text{N}(\text{CH}_2\text{CH}_2\text{OC}_2\text{H}_5)_2$	1

[0267]

[Formula 78]



化合物 No.	M	X	a
C-113	Cu		1
C-114	Cu	$-\text{SO}_2(\text{CH}_2)_2\text{SO}_2\text{NH}(\text{CH}_2)_3\text{OC}_3\text{H}_7(\text{i})$	1
C-115	Cu	$-\text{SO}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$	1
C-116	Cu	$-\text{SO}_2(\text{CH}_2)_2\text{NHCOCH}_2\begin{matrix} \text{C}_2\text{H}_5 \\ \text{C}_4\text{H}_9 \end{matrix}$	1
C-117	Cu	$-\text{SO}_2(\text{CH}_2)_2\text{CO}_2\text{C}_6\text{H}_{13}(\text{n})$	1
C-118	Cu	$-\text{SO}_2\text{C}_6\text{H}_9(\text{n})$	2
C-119	Cu		1
C-120	Cu		1

[0268] The compound expressed with said general formula (C-I) can be compounded if the patent mentioned above is followed. Moreover, the compound expressed with a general formula (C-II) is compoundable by the approach of a publication on each specifications of an application for patent No. 24352 [2000 to], 2000-47013, 2000-57063, and 2000-96610. Moreover, it is not limited by these about starting material, coloring matter intermediate field, and the synthetic root.

[0269] As a content in the ink constituent of the oil solubility coloring matter used for this invention, 0.05 - 50 mass % is desirable to an ink constituent, and 0.1 - 10 mass % is more desirable.

[0270] <High-boiling point organic solvent> Here, the high-boiling point organic solvent used for this invention is explained. The ink constituent of this invention At least one sort of hydrophobic coloring matter, and at least one sort of hydrophobic polymers, At least 1 sort of high-boiling point organic solvent whose solubility of water is 4g or less, and the boiling point are 200 degrees C or less. And after mixing the solution containing at least one sort of auxiliary solvents whose solubility to water is 25g or less, and an aqueous medium and carrying out emulsification distribution, the coloring particle which removes said auxiliary solvent and is obtained is contained. In preparation of said coloring particle, said high-boiling point organic solvent is a component indispensable although the stable coloring particle excellent in the hue is formed. In the coloring particle which said high-boiling point organic solvent is 200 degrees C or more of boiling points, and the melting point is an organic solvent 80 degrees C or less in this invention, and constitutes an ink constituent if the solubility (25 degrees C) of water exceeds 4g In order for big-and-rough-izing, condensation, etc. of the particle diameter in the passage of time to become easy to take place and to do the serious bad operation for the dischargeability of ink, as solubility of water, 4g or less is desirable, 3g or less is more desirable, 2g or less is still more desirable, and especially 1g or less is desirable.

[0271] In this specification, "the solubility of water" is the saturated concentration of the water in the high-boiling point organic solvent in 25 degrees C, and means the mass (g) of the water which can dissolve in 100g of 25-degree C high-boiling point organic solvents.

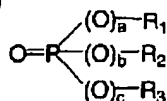
[0272] As amount of the high-boiling point organic solvent used concerning this invention, 5 - 200 mass % is desirable to the coloring matter with which a coloring particle lives together, and 10 - 100 mass % is more desirable.

[0273] In this invention, the compound expressed with [S-9] from the following type [S-1] is desirable as said high-boiling point organic solvent.

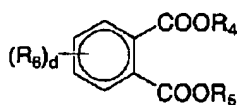
[0274]

[Formula 79]

式 (S-1)



式 (S-2)

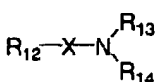


式 (S-3) (Ar-COO)_e-R₇

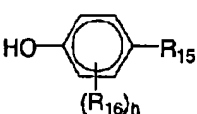
式 (S-4) (R₈-COO)_f-R₉

式 (S-5) R₁₀-(COO-R₁₁)_g

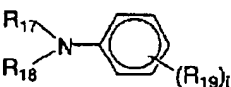
式 (S-6)



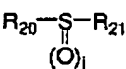
式 (S-7)



式 (S-8)



式 (S-9)



[0275] In said formula [S-1], R1, R2, and R3 express an aliphatic series radical or an aryl group independently respectively. Moreover, a, b, and c express 0 or 1 independently respectively.

[0276] In a formula [S-2], R4 and R5 express an aliphatic series radical or an aryl group independently respectively, R6 expresses a halogen atom (it is the same F, Cl, Br, and below I), an alkyl group, an alkoxy group, an aryloxy group, an alkoxy carbonyl group, or an aryloxy carbonyl group, and d expresses the integer of 0-3. when d is plurality, even if two or more R6 is the same, it may differ.

[0277] In a formula [S-3], Ar expresses an aryl group, e expresses the integer of 1-6 and R7 expresses the hydrocarbon group mutually combined by the hydrocarbon group or ether linkage of e **.

[0278] In a formula [S-4], R8 expresses an aliphatic series radical, f expresses the integer of 1-6 and R9 expresses the hydrocarbon group mutually combined by the hydrocarbon group or ether linkage of f **.

[0279] In a formula [S-5], g expresses the integer of 2-6, R10 expresses the hydrocarbon group (however, an aryl group is removed) of g **, and R11 expresses an aliphatic series radical or an aryl group.

[0280] In a formula [S-6], R12, R13, and R14 express a hydrogen atom, an aliphatic series radical, or an aryl group independently respectively. X expresses -CO- or -SO2-. It may join together mutually and R12, R13, or R13 and R14 may form the ring.

[0281] In a formula [S-7], R15 expresses an aliphatic series radical, an alkoxy carbonyl group, an aryloxy carbonyl group, an alkyl sulfonyl group, an aryl sulfonyl group, an aryl group, or a cyano group, R16 expresses a halogen atom, an aliphatic series radical, an aryl group, an alkoxy group, or an aryloxy group, and h expresses the integer of 0-3. when h is plurality, even if two or more R16 is the same, it may differ.

[0282] In a formula [S-8], R17 and R18 express an aliphatic series radical or an aryl group independently respectively,

R19 expresses a halogen atom, an aliphatic series radical, an aryl group, an alkoxy group, or an aryloxy group, and i expresses the integer of 0-4. when i is plurality, even if two or more R19 is the same, it may differ.

[0283] In a formula [S-9], R20 and R21 express an aliphatic series radical or an aryl group. j expresses 1 or 2.

[0284] Formula [S- When it is the radical in which R1 -R6, and R8, R11-R21 contain an aliphatic series radical or an aliphatic series radical in 1]- [S-9], aliphatic series radicals may be the shape of a straight chain, branched-chain, and annular any, and even if they include the unsaturated bond, they may have the substituent. As an example of a substituent, there are a halogen atom, an aryl group, an alkoxy group, an aryloxy group, an alkoxy carbonyl group, hydroxyl, an acyloxy radical, an epoxy group, etc.

[0285] Formula [S- When R1 -R6, R8, and R11-R21 are annular aliphatic series radicals, i.e., a cycloalkyl radical, in 1]- [S-9] or it is a radical containing a cycloalkyl radical, a cycloalkyl radical may include an unsaturated bond in endocyclic [of 3 - 8 member], and may have the substituent and the bridge formation radical. There are a halogen atom, an aliphatic series radical, hydroxyl, an acyl group, an aryl group, an alkoxy group, an epoxy group, an alkyl group, etc. as an example of a substituent, and methylene, ethylene, isopropylidene, etc. are mentioned as an example of a bridge formation radical.

[0286] Formula [S- When it is the radical in which R1-R6, and R8, R11-R21 contain an aryl group or an aryl group in 1]- [S-9], the aryl group may be permuted by substituents, such as a halogen atom, an aliphatic series radical, an aryl group, an alkoxy group, an aryloxy group, and an alkoxy carbonyl group.

[0287] When R7, R9, or R10 is a hydrocarbon group in a formula [S-3], [S-4], and [S-5], the hydrocarbon group may include cyclic structure (for example, the benzene ring, a cyclopentane ring, a cyclohexane ring) and an unsaturated bond, and may have the substituent. There are a halogen atom, hydroxyl, an acyloxy radical, an aryl group, an alkoxy group, an aryloxy group, an epoxy group, etc. as an example of a substituent.

[0288] Especially a desirable high-boiling point organic solvent is described also in the high-boiling point organic solvent expressed with formula [S-1] - [S-9] below. In a formula [S-1] R1, R2, and R3 respectively -- becoming independent -- the aliphatic series radical (for example, n-butyl --) of the carbon atomic numbers (it abbreviates to C number below) 1-24 (preferably 4-18) 2-ethylhexyl, 3 and 3, 5-trimethylhexyl, n-dodecyl, n-octadecyl, benzyl, oleyl one, 2-chloro ethyl, 2, 3-dichloro propyl, 2-butoxy ethyl, 2-phenoxy ethyl, cyclopentyl, cyclohexyl, It is an aryl group (for example, phenyl, cresyl, p-nonylphenyl, the xylyl, KUMENIRU, p-methoxyphenyl, p-methoxycarbonyl phenyl) with 4-t-butyl cyclohexyl, 4-methylcyclohexyl, or 6-24 (preferably 6-18) C. a, b, and c -- each -- independent -- 0 or 1 - - it is -- more -- desirable -- a, b, and c -- it is 1 altogether.

[0289] a formula [S-2] -- setting -- R4 and R5 -- an aliphatic series radical (for example, the same radical as the alkyl group mentioned about said R1 --) with 1-24 (preferably 4-18) C Ethoxy carbonylmethyl, 1, and 1-diethyl propyl, 2-ethyl-1-methyl hexyl, Cyclohexyl methyl, 1-ethyl -1, 5-dimethyl hexyl, 3 and 5, 5-trimethyl cyclohexyl, an aryl group (for example, the aryl group mentioned about said R1 --) with menthyl, bornyl one, 1-methylcyclohexyl, or 6-24 (preferably 6-18) C 4-t-buthylphenyl, 4-t-octyl phenyl, 1 and 3, 5-trimethyl phenyl, They are 2, 4, - G t-buthylphenyl, 2 and 4, and - G t-pentyl phenyl. R6 -- an alkyl group (for example, methyl --) with a halogen atom (preferably chlorine atom) and 1-18 C an alkoxy group with isopropyl, t-butyl, n-dodecyl, and 1-18 C (for example, methoxy --) n-butoxy, n-octyloxy, methoxyethoxy one, benzyloxy, an aryloxy group with 6-18 C (for example, phenoxy and p-tolyloxy --) an alkoxy carbonyl group with 4-methoxy phenoxy, 4-t-butyl phenoxy, or 2-19 C (for example, methoxycarbonyl --) It is n-butoxycarbonyl, 2-ethylhexyloxy carbonyl, or an aryloxy carbonyl group with 6-25 C, and d is 0 or 1.

[0290] a formula [S-3] -- setting -- Ar -- an aryl group (for example, phenyl --) with 6-24 (preferably 6-18) C 4-chlorophenyl, 4-methoxyphenyl, 1-naphthyl, 4-n-butoxy phenyl, It is 1, 3, and 5-trimethyl phenyl, and e is the integer of 1-4 (preferably 1-3). R7 -- a hydrocarbon group with 2-24 (preferably 2-18) C of e ** -- [-- the alkyl group mentioned about said R4, a cycloalkyl radical, an aryl group, -(CH2) 2-, and [0291] [for example,]

[Formula 80]

[0299] a formula [S-6] -- setting -- R12 -- a hydrogen atom and an aliphatic series radical with 1-24 C (preferably 3-20) -- [-- for example, n-propyl -- 1-ethyl pentyl, n-undecyl, n-pentadecyl, 2, 4-G t-pentyl phenoxyethyl, 4-t-octyl

phenoxymethyl, 3-(2, 4-G t-butyl phenoxy) propyl, 1-(2, 4-G t-butyl FEKISHI) propyl, cyclohexyl, It is an aryl group (for example, aryl group mentioned about said Ar) with 4-methylcyclohexyl or 6-24 (preferably 6-18) C. R13 and R14 a hydrogen atom and an aliphatic series radical (for example, methyl --) with 1-24 (preferably 1-18) C It is an aryl group (for example, phenyl, 1-naphthyl, p-tolyl) with ethyl, isopropyl, n-butyl, n-hexyl, 2-ethylhexyl, n-dodecyl, cyclopentyl, cyclo propyl, or 6-18 (preferably 6-15) C. R13 and R14 may join together mutually, a pyrrolidine ring, a piperidine ring, and a morpholine ring may be formed with N, and R12 and R13 may join together mutually, and may form a pyrrolidone ring. X is -CO- or -SO2- and X is -CO- preferably.

[0300] a formula [S-7] -- setting -- R15 -- an aliphatic series radical (for example, methyl --) with 1-24 (preferably 3-18) C Isopropyl, t-butyl, t-pentyl, t-hexyl, t-octyl, 2-butyl, 2-hexyl, 2-octyl, 2-dodecyl, 2-hexadecyl, t-pentadecyl, cyclopentyl, cyclohexyl, and an alkoxy carbonyl group (for example, n-butoxycarbonyl --) with 2-24 (preferably 5-17) C an alkyl sulfonyl group (for example, a methyl sulfonyl --) with 2-ethylhexyloxy carbonyl and 1-24 (preferably 1-18) n-dodecyloxy carbonyl C an aryl sulfonyl group (for example, p-tolyl sulfonyl --) with n-butyl sulfonyl, n-dodecyl sulfonyl, and 6-30 (preferably 6-24) C p-dodecyl phenyl sulfonyl, p-hexadecyl oxy-phenyl sulfonyl, an aryl group (for example, phenyl --) with 6-32 (preferably 6-24) C They are p-tolyl or a cyano group. R16 A halogen atom (preferably Cl), An alkyl group with 1-24 (preferably 1-18) C (for example, alkyl group mentioned about said R15), a cycloalkyl radical (for example, cyclopentyl --) with 3-18 (preferably 5-17) C an aryl group (for example, phenyl --) with cyclohexyl and 6-32 (preferably 6-24) C an alkoxy group (for example, methoxy --) with 1-24 (preferably 1-18) p-tolyl C n-butoxy, 2-ethylhexyloxy, benzyloxy one, n-dodecyloxy, an aryloxy group (for example, phenoxy --) with n-hexadecyl oxy-or 6-32 (preferably 6-24) C It is p-t-butyl phenoxy, p-t-octyl phenoxy, m-pentadecyl phenoxy, and p-dodecyloxy phenoxy, and h is the integer of 1-2.

[0301] In a formula [S-8], R17 and R18 are the same as said R13 and R14, and R19 is the same as said R16.

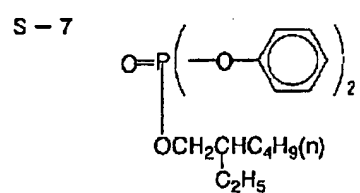
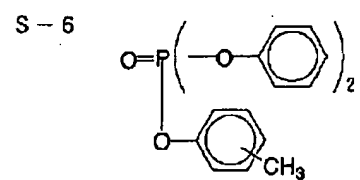
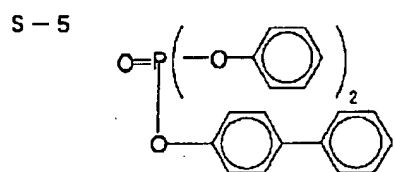
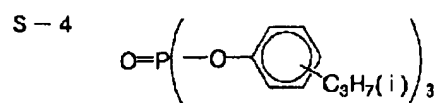
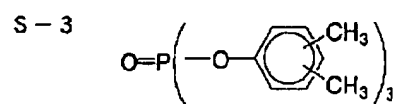
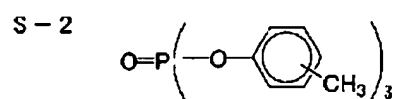
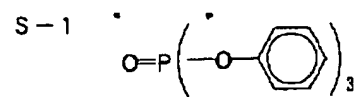
[0302] In a formula [S-9], R20 and R21 are the same as said R1, R2, and R3. j expresses 1 or 2 and j is 1 preferably.

[0303] The example (S-1-93) of the high-boiling point organic solvent used for below in this invention is shown.

[0304]

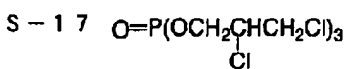
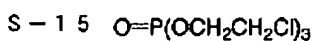
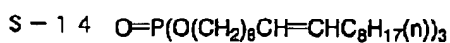
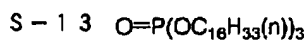
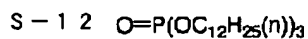
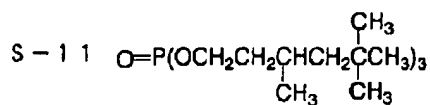
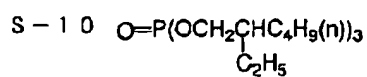
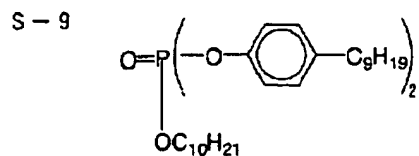
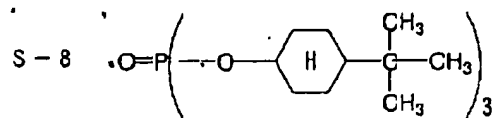
[Formula 83]

式〔S-1〕で表される化合物



[0305]

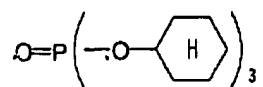
[Formula 84]



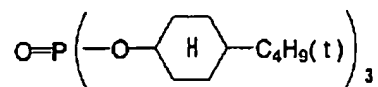
[0306]

[Formula 85]

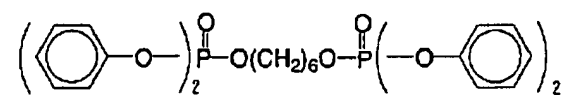
S - 1 8'



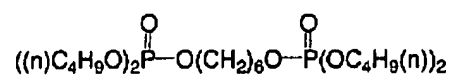
S - 1 9



S - 2 0



S - 2 1



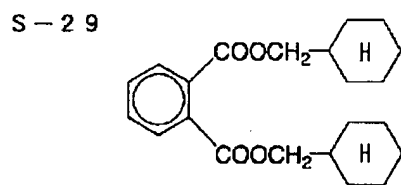
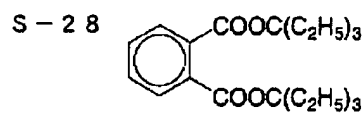
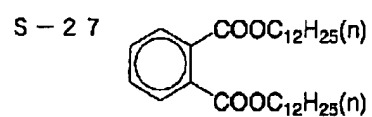
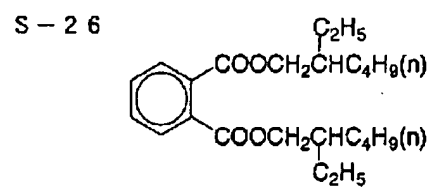
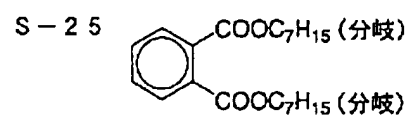
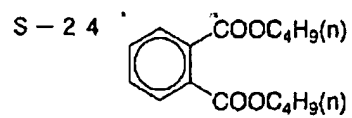
S - 2 2 $((\text{n})\text{C}_8\text{H}_{17})_3\text{P}=\text{O}$

S - 2 3 $(\text{n})\text{C}_8\text{H}_{17}\text{---}\text{P}(=\text{O})(\text{OC}_8\text{H}_{17}(\text{n}))_2$

[0307]

[Formula 86]

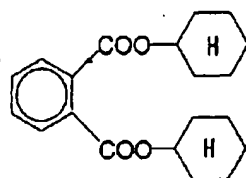
式〔S-2〕で表される化合物



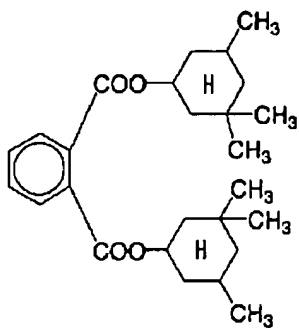
[0308]

[Formula 87]

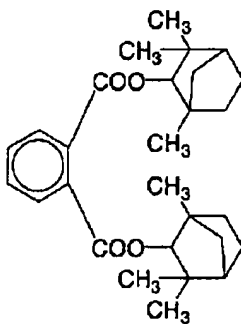
S - 3 0



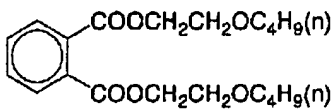
S - 3 1



S - 3 2



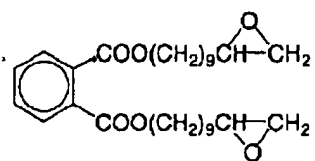
S - 3 3



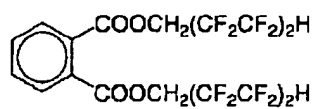
[0309]

[Formula 88]

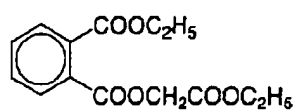
'S - 3 4'



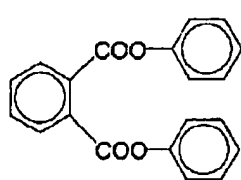
S - 3 5



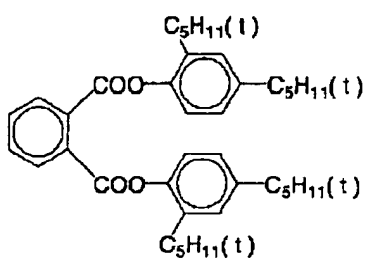
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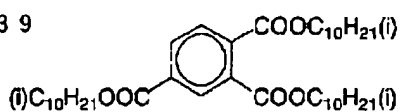
S - 3 7



S - 3 8



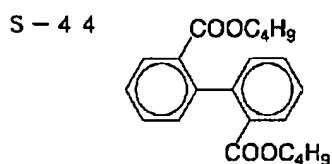
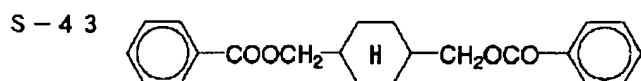
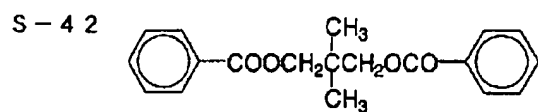
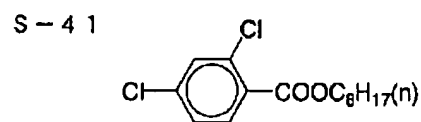
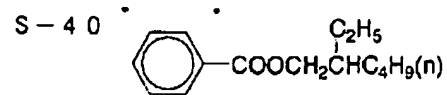
S - 3 9



[0310]

[Formula 89]

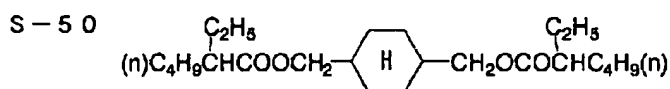
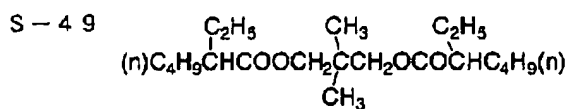
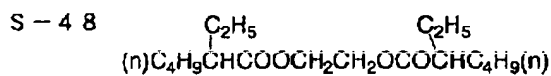
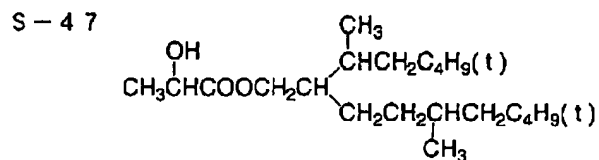
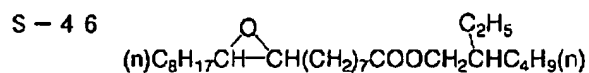
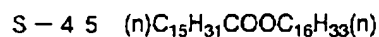
式〔S-3〕で表される化合物



[0311]

[Formula 90]

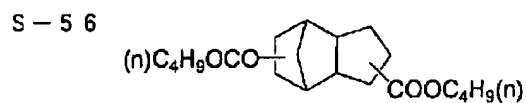
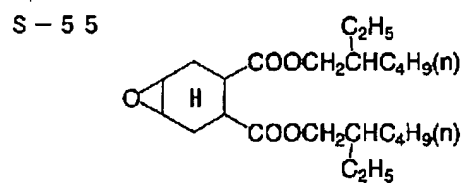
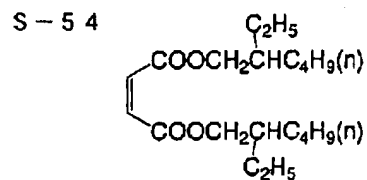
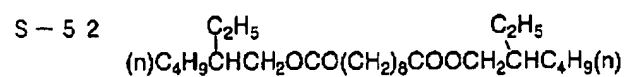
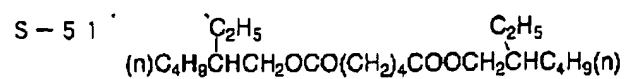
式〔S-4〕で表される化合物



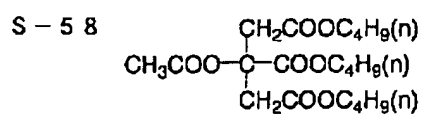
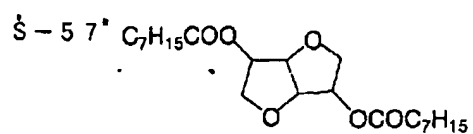
[0312]

[Formula 91]

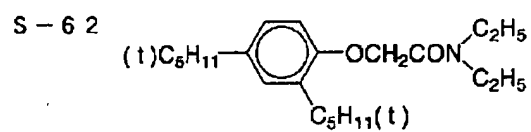
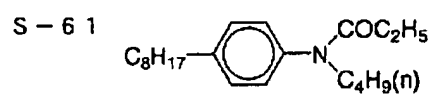
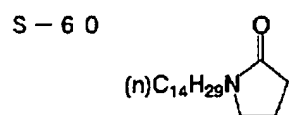
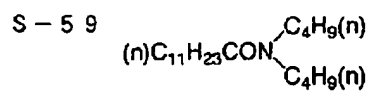
式〔S-5〕で表される化合物



[0313]
[Formula 92]

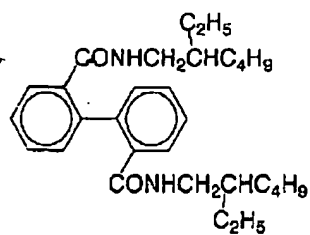


式〔S - 6〕で表される化合物

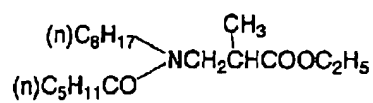


[0314]
[Formula 93]

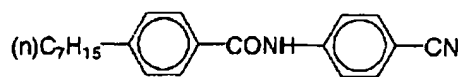
S - 6 3'



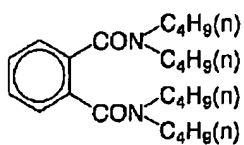
S - 6 4



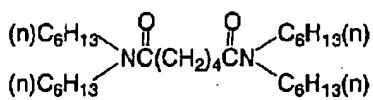
S - 6 5



S - 6 6



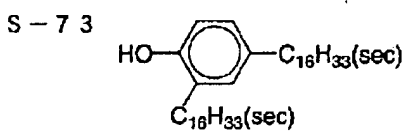
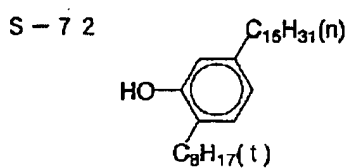
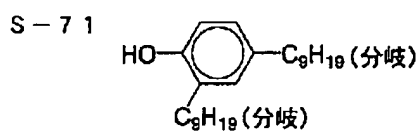
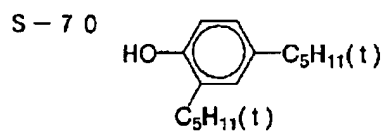
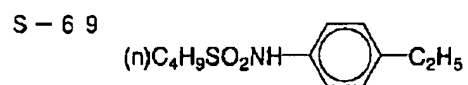
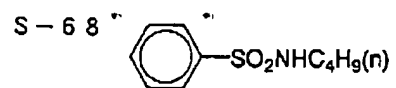
S - 6 7



[0315]

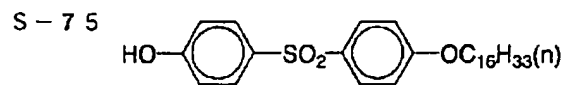
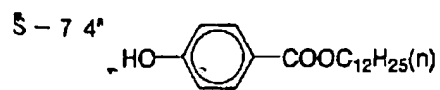
[Formula 94]

式〔S-7〕で表される化合物

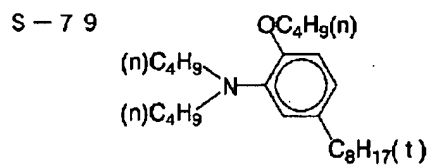
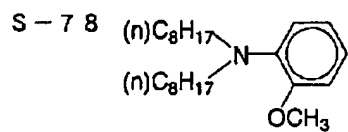
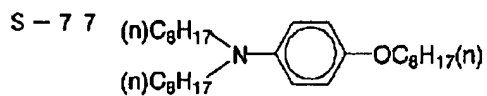
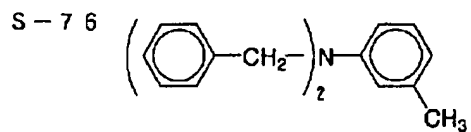


[0316]

[Formula 95]



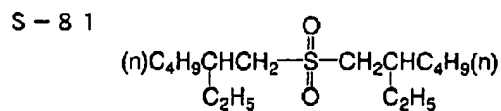
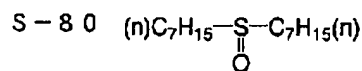
式〔S-8〕で表される化合物



[0317]

[Formula 96]

式〔S-9〕で表される化合物

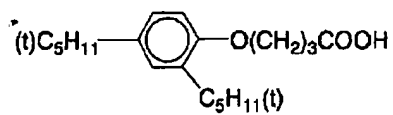


[0318]

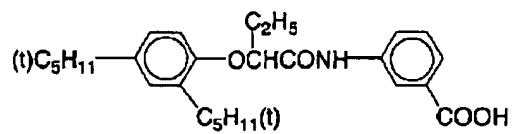
[Formula 97]

その他の化合物

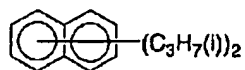
S - 8 2



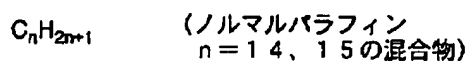
S - 8 3



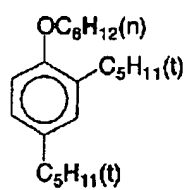
S - 8 4



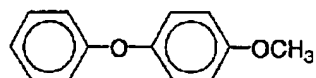
S - 8 5



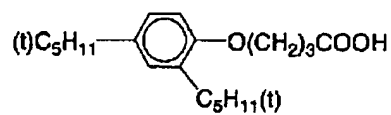
S - 8 6



S - 8 7



S - 8 8



[0319]

[Formula 98]

その他の化合物

S-89 塩素化パラフィン (平均組成 $C_{14}H_{24}Cl_6$)

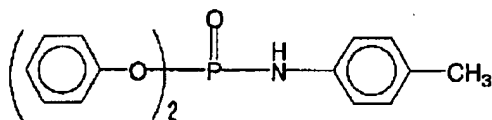
S-90 塩素化パラフィン (平均組成 $C_{12}H_{18}Cl_6$)

S-91 ポリ (クロロトリフルオロエチレン)
(平均分子量 900)

S-92



S-93



[0320] In this invention, a high-boiling point organic solvent may use one kind independently, or may use it by mixing (for example, tricresyl phosphate, dibutyl phthalate and trioctylphosphate, di(2-ethylhexyl) sebacate and dibutyl phthalate, and Pori (N-t-butyl acrylamide) []) Carrying out two or more sorts.

[0321] In this invention, as a mass ratio of said hydrophobic coloring matter and said high-boiling point organic solvent, it is desirable that a hydrophobic coloring matter:high-boiling point organic solvent is 1:0.01-1:1, and it is more desirable that it is 1:0.05 to 1:0.5.

[0322] About examples of a compound other than [said] the high-boiling point organic solvent used in this invention, and/or the synthetic approach of these high-boiling point organic solvent For example, U.S. Pat. No. 2,322,027, 2,533,514, 2,772,163, 2,835,579, 3,594,171, 3,676,137, 3,689,271, 3,700,454, 3,748,141, 3,764,336, 3,765,897, 3,912,515, 3,936,303, 4,004,928, 4,080,209, 4,127,413, 4,193,802, 4,207,393, 4,220,711, 4,239,851, 4,278,757, 4,353,979, 4,363,873, 4,430,421, 4,430,422, 4,464,464, 4,483,918, 4,540,657, 4,684,606, 4,728,599, 4,745,049, 4,935,321, 5,013,639 and the Europe patent 276,319th -- No. A -- said -- the 286,253rd -- No. A said -- the 289,820th -- No. A -- said -- the 309,158th -- No. A -- said -- the 309,159th -- No. A said -- the 309,160th -- No. A -- said -- the 509,311st -- No. A -- said -- the 510,576th -- No. A The East Germany patent No. 147,009, 157,147, 159,573, said -- the 225,240th -- No. A and the British patent 2,091,124th -- each specification, such as No. A, -- JP,48-47335,A, 50-26530, 51-25133, 51-26036, 51-27921, 51-27922, 51-149028, 52-46816, 53-1520, 53-1521, 53-15127, 53-146622, 54-91325, 54-106228, 54-118246, 55-59464, 56-64333, 56-81836, 59-204041, 61-84641, 62-118345, 62-247364, 63-167357, 63-214744, 63-301941, 64-9452, 64-9454, It is indicated by each official report, such as 64-68745, JP,1-101543,A, 1-102454, 2-792, 2-4239, 2-43541, 4-29237, 4-30165, 4-232946, and 4-346338.

[0323] A <auxiliary solvent>, next the auxiliary solvent used for this invention are explained. In this invention, an auxiliary solvent is used with said high-boiling point organic solvent. This auxiliary solvent is a low-boiling point solvent or an organic solvent of dissolved water in fuel, and is a solvent removed with evaporation, film dialysis, an ultrafiltration, etc. after emulsification distribution. When preparing the coloring particle concerning this invention which contains hydrophobic coloring matter, a hydrophobic polymer, and a high-boiling point organic solvent at least, in order for distribution of grain size to obtain a stable distributed object narrowly, the one where the solubility to the water of said auxiliary solvent is smaller is desirable. On the other hand, in order to make an auxiliary solvent easy to remove smoothly after emulsification distribution, the solubility to water is needed to some extent. Therefore, it is not desirable in order to obtain the stable water and distribution object of distribution of grain size with completely narrow

the solvent of a miscibility, for example, methanol, ethanol, isopropyl alcohol, acetone, etc. As solubility (as opposed to 25 degrees C and 100g of water) to the water of said auxiliary solvent concerning this invention, 0.5 or more g [25] or less is desirable, and 1g or more 20g or less is more desirable. Although the desirable example (AS-1-11) of said auxiliary solvent and the solubility to those water are shown below, this invention is not limited to these at all.

[0324]

Auxiliary solvent Solubility to the water of an auxiliary solvent (25 degrees C)

AS-1 Ethyl acetate 8g AS-2 Propyl acetate 2g AS-3 Acetic-acid 2-ethyl butyl <1g AS-4 Acetic-acid 2-ethylene 20g AS-5 2-ethoxyethyl acetate 25g AS-6 Butyl acetate 2g AS-7 Ethyl propionate 2g AS-8 Acetylacetone 12g AS-9 Ethyl acetoacetate 12g AS-10 2-(2-n-butoxyethoxy) ethyl acetate 2g AS-11 Cyclohexanone 15g [0325] The amount of one to 200 times is desirable to the coloring matter which lives together in a coloring particle as amount of the auxiliary solvent used in this invention, and the amount of two to 100 times is more desirable.

[0326] <Hydrophobic polymer> Here, the hydrophobic polymer used for this invention is explained. The coloring particle contained in the ink constituent of this invention contains at least one sort of hydrophobic coloring matter, and at least one sort of hydrophobic polymers. The polymer which is one of the components which constitute said coloring particle and by which the polymer obtained by the polycondensation is also obtained from a vinyl monomer as structure of a hydrophobic polymer is sufficient.

[0327] The homopolymer of the monomer of arbitration chosen from the monomer group shown as an example below as a hydrophobic polymer concerning this invention may be used, and the copolymer which combined the monomer of arbitration freely may be used. Moreover, there is especially no limit in an usable monomeric unit, and the thing of arbitration is usable if a polymerization is possible by the usual radical polymerization method.

[0328] As a polymer obtained by said polycondensation, a polyester system polymer is desirable, for example, consists of multiple-valued carboxylic acids and polyhydric alcohol, and independent or the resin which carried out the polymerization combining two or more kinds of monomers is mentioned.

[0329] Especially as said multiple-valued carboxylic acids, although not limited For example, a terephthalic acid, isophthalic acid, an orthochromatic phthalic acid, 1, 5-North America Free Trade Agreement RUREN dicarboxylic acid, 2, 6-naphthalene dicarboxylic acid, diphenic acid, a sulfo terephthalic acid, 5-sulfoisophtharate, 4-sulfo phthalic acid, 4-sulfo naphthalene -2, 7 dicarboxylic acid, 5 [4-sulfo phenoxy] isophthalic acid, a sulfo terephthalic acid, a p-oxy-benzoic acid, p-(hydroxy ethoxy) benzoic acid, a succinic acid, an adipic acid, an azelaic acid, A sebacic acid, dodecane dicarboxylic acid, boletic acid, a maleic acid, an itaconic acid, Hexahydrophthalic acid, a tetrahydrophthalic acid, trimellitic acid, trimesic acid, The aromatic series multiple-valued carboxylic acid shown with pyromellitic acid etc., aromatic series hydroxy acid, aliphatic series dicarboxylic acid, alicycle group dicarboxylic acid, etc. are mentioned, and these can be used also as a metal salt, ammonium salt, etc.

[0330] Especially as polyhydric alcohol, although not limited For example, ethylene glycol, propylene glycol, 1,3-propanediol, 2, 3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, a diethylene glycol, Dipropylene glycol, 2 and 2, 4-trimethyl -1, 3-pentanediol, A polyethylene glycol, a polypropylene glycol, a polytetramethylene glycol, Trimethylolethane, trimethylol propane, a glycerol, a pen TAERUSURI toll, 1, 4-cyclohexane diol, 1, 4-cyclohexane dimethanol, Spiroglycol, tricyclodecane diol, tricyclodecane dimethanol, The aliphatic series polyhydric alcohol shown by a meta-xylene glycol, an alt.xylene glycol, 1, 4-phenylene glycol, bisphenol A, lactone system polyester, and polyols, alicycle group polyhydric alcohol, and aromatic series polyhydric alcohol are mentioned. Moreover, what closed the polar group of the end of a macromolecule chain can also be used for said multiple-valued carboxylic acids and said polyhydric alcohol of independence, or the polyester resin which combined two or more kinds and carried out the polymerization using the compound which is usually known and in which end closure is possible.

[0331] The homopolymer of the monomer of arbitration chosen from the monomer group shown as an example below as a polymer obtained from said vinyl monomer is sufficient, and the copolymer which combined the monomer of arbitration freely is sufficient. There is especially no limit in an usable monomeric unit, and the object of arbitration is usable if a polymerization is possible by the usual radical polymerization method. Moreover, although the example of a monomer is given to below, this invention is not limited to these at all.

[0332] As said monomer group, the derivative of olefins, alpha, and beta-unsaturated-carboxylic-acid and its salts, alpha, and beta-unsaturated carboxylic acid, alpha, the amides of beta-unsaturated carboxylic acid, styrene and its derivative, vinyl ether, vinyl ester, other polymerization nature monomers, etc. are mentioned, for example.

[0333] As said olefins, ethylene, a propylene, an isoprene, a butadiene, a vinyl chloride, a vinylidene chloride, a 6-hydroxy-1-hexene, a cyclopentadiene, 4-pentene acid, 8-nonene acid methyl, a vinyl sulfonic acid, trimethyl vinylsilane, trimethoxy vinylsilane, a butadiene, pentadiene, an isoprene, 1, 4-divinyl cyclohexane, 1 and 2, 5-TORIBI nil cyclohexane, etc. are mentioned.

[0334] As Above alpha, beta-unsaturated carboxylic acid, and its salts, an acrylic acid, a methacrylic acid, an itaconic

acid, a maleic acid, acrylic-acid sodium, methacrylic-acid ammonium, an itaconic-acid potassium, etc. are mentioned. [0335] As a derivative of Above alpha and beta-unsaturated carboxylic acid alkyl acrylate (for example, methyl acrylate and ethyl acrylate --) n-butyl acrylate, cyclohexyl acrylate, 2-ethylhexyl acrylate, Permutation alkyl acrylate, such as n-dodecylacrylate for example, 2-chloro ethyl acrylate and benzyl acrylate -- Alkyl methacrylate, such as 2-cyano ethyl acrylate and allyl compound acrylate (methyl methacrylate, n-butyl methacrylate, 2-ethylhexyl methacrylate, n-dodecyl methacrylate, etc. and permutations) alkyl methacrylate [-- for example, [for example,] 2-hydroxyethyl methacrylate, glycidyl methacrylate, Glycerol mono-methacrylate, 2-acetoxy ethyl methacrylate, Tetrahydrofurfuryl methacrylate, 2-methoxy ethyl methacrylate, omega-methoxy polyethylene-glycol methacrylate (the number of addition mols of a polyoxyethylene = thing of 2-100), Polyethylene glycol monomethacrylate (the number of addition mols of a polyoxyethylene = thing of 2-100),

Since it became timeout time, translation result display processing is stopped.